A contribution on the bio-actions of rare earth elements in the soil/plant environment

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Dedication

I didicate this work to my great mother Nozha, my great father Ragab, my lovely wife Neama, my handsome sons Mahmoud and Abd El-Rahman.

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1 Introduction

It is well known that rare earth elements (REEs) comprise a homogenous group of elements in the Periodic Table. They include the elements scandium (Sc), yttrium (Y) and 15 lanthanides with successive atomic numbers from 57 to 71. The lanthanides consist of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) (Hu et al., 2004).

Yttrium (atomic number 39), a Group IIIA transition metal, although not a lanthanide is generally included with the REEs as it is occurs with them in natural minerals and has similar chemical properties. Commonly included with REEs, because of their similar properties, is scandium (atomic number 21), also a Group IIIA transition metal. In some classification schemes, the lanthanides are termed "rare earth elements", which includes the additional elements (Y) and (Sc), because these two metals and the lanthanides possess similar chemical and toxicological properties, and they occur together with the lanthanides in ores. In geochemistry, the term "rare earth elements" generally refers only to the lanthanides (La-Lu), and this well entrenched distinction from chemical nomenclature has been the source of some confusion. Christie et al. (2001) reported about the mineralogy, geochemistry and occurrence of REEs. The history of the discovery and naming of REEs was reviewed by many researchers (e.g. Evans, 1990, Habashi 1994a and Habashi 1994b) while, Horovitz (1999) and Horovitz (2000) reported about the history of Sc and Y (Table 1.1 and see Appendix).

The total world reserves are an estimated 100 million metric tons of REO and the regions having major ore reserves are China (43%), commonwealth of Independent States (19%), United States (13%), Australia (5.2%), India (1.1%), Canada (0.94%), South Africa (0.39%), and Brazil (0.08%). Most REEs are produced from bastnaesite, monazite and xenotime (Giungato and Notarnicola, 2003). In Table 1.2, the world production of rare earth mineral concentrations from 2001 to 2006 is tabulated.

The Chinese fertilizer industry produces a total of 5 million tons of REEs ammonium carbonate fertilizer, which is able to supply the requirements of 6.68 million ha of farmland (Anon, 1998). The rare earth consumption for agricultural purposes has reached 1,100 tons REEs (expressed as oxides, REO) per year, with agriculture becoming one of the leading REEs demanding branches in China (Yan, 1999). China's mine production was 73,000 tons REO in 2000 and 75,000 tons REO in 2001. This corresponded to 87% and 90% of the world's production in the periods. In 2002, the world production of REO (REEs as oxide) was 88,000 tons, with China alone contributing about 90% of this production (Di Francesco and Hedrick, 2004). Figure (1.1) shows the global REEs production from 1950 until 2000 (Haxel et al., 2004).

Table 1.1: Discovery and origins of names of REEs (Evans 1990 and Christie et al., 2001)

REEs	Origin of name	Discovery	Nationality (Year)	Comment (The meaning)
Y	Ytterby mine, Sweden	Gadolin	Finnish (1794)	A silvery metallic element that is common in rare-earth minerals; used in magnesium and aluminium alloys.
Ce	After the asteroid Ceres (which in turn named after a Greek deity)	Baron Jones Jakob Berzlius and William Hisinger	Swedish (1804)	Also discovered independently in same year by Martin Heinrich (German). The pure element was not isolated until 1875.
La	From Greek lanthno = to lie hidden (because it lay concealed in the earth)	Carl Gustav Mosander	Swedish (1839)	A white soft metallic element that tarnishes readily; occurs in rare earth minerals and is usually classified as a rare earth.
Er	Derived from Ytterby mine, Sweden	Carl Gustav Mosander	Swedish (1843)	A trivalent metallic element of the rare earth group; occurs with yttrium.
Tb	Derived from Ytterby mine, Sweden	Carl Gustav Mosander	Swedish (1878)	A metallic element of the rare earth group; used in lasers; occurs in apatite and monazite and xenotime and ytterbite.
Sm	After the mineral Samarskite, in turn after the minerals discoverer, a Russian mining official V.E. Samarsky	Paul E. Lecoq de Boisbaudran	French (1879)	A gray lustrous metallic element of the rare earth group; is used in special alloys; occurs in monazite and Bastnaesite.
Sc	After Scandinavia	Lars Fredrik Nilson	Swedish (1879)	A white trivalent metallic element; occurs in the Scandinavian mineral Thortveitite.
Ho	After the Latin for Stockholm, Holmia	Per Teodor Cleve	Swedish (1879)	Discovered independently by Jacques Louis Soret and Marc Delafontaine (Swiss)
Tm	From the Latin Thule, an ancient name for Scandinavian	Per Teodor Cleve	Swedish (1878)	A soft silvery metallic element of the rare earth group; it occurs in monazite, apatite and Xenotime.
Gd	In honor of Johan Gadolin, a Finnish chemist	Jean de Marignac	Swiss (1880)	Paul E. Lecoq de Boisbaudran independently isolated the element from Meander's "yttria" in 1886.
Pr	From Greek prasios = green, in reference to the color of the salts, and didymos = twin, because the earth didymia was separated into two salts; Pr and Nd	Carl Auer von Welsbach	Austrian (1885)	The meaning: a soft yellowish-white trivalent metallic element of the rare earth group; can be recovered from Bastnaesite or monazite by an ion-exchange process.

Table 1.1: Cont.

Nd	From Greek neo = new and didymos = twin, because the earth didymia was separated into two salts; Pr and Nd	Baron Carl Auer von Welsbach	Austrian (1885)	Not isolated in relatively pure form until 1925. a yellow trivalent metallic element of the rare earth group; occurs in monazite and Bastnaesite in association with Ce, La and praseodymium.
Dy	From Greek dys = bad and prositos = approachable, dysprositos means hard to get because of the difficulty involved in its detection and isolation	Paul E. Lecoq de Boisbaudran	French (1886)	The meaning: a trivalent metallic element of the rare earth group; forms compounds that are highly magnetic.
Eu	After Europe	Eugène Demarcay	French (1896)	A bivalent and trivalent metallic element of the rare earth group.
Lu	After Lutetia, Latin name for the place where Paris was founded	Independently by Georges Urbain and Carl Auer von Welsbach	French and Austrian (1907)	A trivalent metallic element of the rare earth group; usually occurs in association with yttrium.
Pm	After Prometheus, in Greek mythology, who brought fire to mankind in reference to harnessing of the energy of the nuclear fission and warning against its dangers	Charles Du Bois Coryell, Lawrence E. Glendenin and Jacob A. Marinsky	American (1945)	A soft silvery metallic element of the rare earth group having no stable isotope; was discovered in radioactive form as a fission product of uranium.

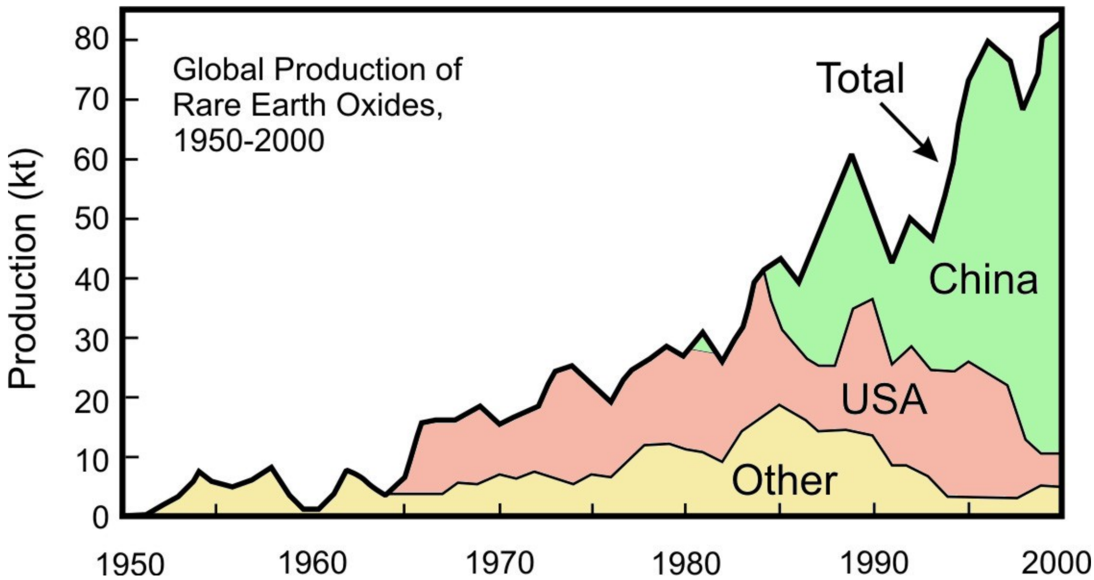


Figure 1.1: Global REE production (1kt =10^6 kg) from 1950 through 2000 (adapted from Haxel et al., 2004)

Table 1.2: World mine production, reserves and reserve base of REEs (Hedrick, 2007)

Country	Mine production (10^3 t)						Reserves (2006)	Reserve Base (2006)
	2001	2002	2003	2004	2005	2006	(10^3 t)	(10^3 t)
United States	5	5	5	5	-	-	13,000	14,000
Australia	-	-	-	-	-	-	5,200	5,800
Brazil	0.2	-	-	-	-	-	-	-
Thailand	-	-	2.2	2.2	-	-	ND	ND*
China	75	88	92	95	119	120	27,000	89,000
India	2.7	2.7	2.7	2.7	2.7	2.7	1,100	1,300
Malaysia	0.5	0.5	0.3	0.3	0.3	0.2	30	35
C. I. S.	2.0	2.0	2.0	2.0	2.0	ND	19,000	21,000
Sri Lanka	0.1	0.1	-	-	-	-	-	-
Other countries	-	-	-	-	0.4	0.4	22,000	23,000
World total (rounded)	85.5	98.3	99.1	102	123	123	88,000	150,000

* ND, not detected.
C. I. S. = Commonwealth of Independent States (Kazakhstan, Kirghizia, Russia and Ukraine).
Reserves, it means the part of the reserve base, which could be economically extracted or produced at the time of determination.
Reserve Base: that part of an identified resource that meets specific minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness and depth.

Beneficial and toxic effects of REEs

Until recently, the REEs have neither been characterized as essential elements for life, nor as strongly toxic elements in the environment. Much less interest has, therefore, been paid to them than to several transition and other heavy metals. Several interactions between REEs and biological systems are known. Many studies in Chinese agricultural science have suggested, indicated or even demonstrated that low concentrations of REEs may promote growth and productivity of several crops. Application of these elements, either to the seed or to the crop biomass is nowadays widely practiced in Chinese agriculture, thus in a considerable part of the earth's cultivated soils. The physiological and ecophysiological mechanisms underlying their reactions have recently been given much attention. However, there are conflicting evidence and opinions regarding the importance of REEs in pedology and biology. During the last decade much new information has appeared on the occurrence, behavior and possible biological role of REEs in soil and plant systems (Tyler, 2004).

The diverse nuclear, metallurgical, chemical, catalytic, electric, magnetic, and optical properties of REEs have led to an increasing variety of applications over the past four decades. Due to the increasing demand, the global REEs annual production has grown from several thousand tones in 1950 up to almost 100,000 tones in 2000. It can be expected that emissions of REEs to the environment have increased in a similar manner. REEs are also contained in appreciable quantities in phosphate fertilizers, the use of which has also considerably grown over the past decades. These facts have led to an increasing concern about the impact of REEs on the environment (See Appendix). For instance, maximum permissible concentrations of some of REEs for surface water, sediment and soil have recently been established in The Netherlands (Sneller et al., 2000); (Kučera et al., 2007).

In China, scientists have applied inorganic compounds of rare earths such as $RE(NO_3)_3$, which act as a microelement fertilizer, to agricultural crops and studied their effects on crop yield and quality. They have also studied cumulative concentrations of REEs in the field since the 1970s (Wang et al., 2003d). Chinese researchers have reported beneficial effects of low doses of REEs on a wide range of crops growing in soils, for example, when applied as foliar sprays, seed treatments, or added to solid or liquid rooting media (Guo 1987; Xiong 1995; Xie et al., 2002). However, these beneficial effects have seldom been reported in other countries. In contrast, the REEs have been shown to be highly toxic to plants (Diatloff et al., 1995a,b; Hu et al., 2002) and microorganisms (Chu et al., 2003a; Tang et al., 2004). The harmful effects of excessive REEs on soil microbial biomass (Chu et al., 2001b), N transformations (Xu and Wang 2001; Zhu et al., 2002), CO_2 evolution, and enzyme activities (Chu et al., 2003b; Xu et al., 2004) have been reported in several studies. Until now, however, the application of REEs to soil has not been limited in China, and therefore, there is growing concern about the adverse effects of the accumulation of REEs in soils (Chu et al., 2007).

In this study the dose/effect relationships were tested for La and Ce, a REE fertilizer and compared to that of other heavy metals, copper and an essential plant nutrient, Ca. Calcium was chosen because of its suggested similarity with La.

The main objectives of this study were:

(I) To study the dose/effect relationships of added REEs on soil microbiological parameters (soil enzyme activities and microbial counts) using maize and oilseed rape crops in order to understand the environmental chemistry behaviors of REEs as fertilizers in soils.

(II) To determine dose/effect relationships of added REEs on the growth parameters of maize and oilseed rape crops and REEs bioaccumulation.

(III) To evaluate the chances and ecotoxicological risks of REEs in agricultural environment.

2 Literature review of REEs in the environment

Historical background and discovery of REEs

The history of the discovery of REEs is one of the most complex and confusing areas in inorganic chemistry and has produced two hundred years of trial, error and false claims which reflect its peculiar nature within the periodic system. As REEs could not be properly arranged into any table, no information on the number of existing elements was available. Thus, fractional crystallization was the only method used for the purification of elements at that time and multiple recrystallizations were necessary that in turn caused various false claims on the nature of REEs (Holden, 2001).

The history of REEs began in 1787. *Carl Axel Arrhenius*, a lieutenant of the Swedish Royal Army, was a gifted, though amateur, mineralogist. At an excursion in the vicinity of Ytterby, a small Swedish town three miles away from Stockholm, he found a curious black mineral that had never before been mentioned by anyone. He just called “black stone”. Ever since, many REEs bear the name of town Ytterby. As new elements again and again turned up from analyzing the back mineral, the discoverers gave them names by varying the name Ytterby: yttrium, ytterbium, terbium, erbium all stem from it. The new mineral was first studied by an acquaintance of Arrhenius, Bengt Reinhold Geijer. He was the first to report on it in the literature. He assumed that the asphalt-like mineral contained tungsten, by reason of its high density. The next scientist who took interest in the mineral was a Finnish chemist, Johan Gadolin. He analyzed it in 1794 and found a new “earth” in it that was similar in many respects to alumina and also to lime (Szabadvary, 1988).

Table 2.1 shows the main historical events related to research and application of REEs in agriculture (see also Tables A.1 and A.2 in Appendix). The pioneer study of REEs effects on plants was published by Chien and Ostenhout (1917) who reported on the effects of barium (Ba), strontium (Sr), and cerium (Ce) on water-floss (*Spirogyra*). Soviet scientists, Romanian, Bulgarian and Chinese researchers reported on the effects of REEs as shown in Table 2.1. The first country in the world to use commercial REEs-fertilizers for crop production was China, a process that began in 1980s with field experiments and increased rapidly (Hu et al., 2004). Some fertilizers containing REEs have been applied in China to improve crop production and are estimated to cover approximately 3.7×10^6 ha in 1993 and $1.6–2.0\times10^7$ ha in 1995 (Diatloff et al., 1996; Ni, 1995). Little attention has been paid to the accumulation of REEs in crops after years of application. For the safety assessment of agricultural application of REEs, it is important to study the dose-dependent accumulation of individual REEs in crops upon addition of such fertilizers, and the corresponding mechanisms by which the REEs can enter the plants (Xu et al., 2003a).

Table 2.1: Milestones in agricultural research on REEs (adapted from Hu et al., 2004)

Year	Incidents	References
1917	Detection of physiological effects of Ce on Spirogyra.	Chien and Ostenhout (1917)
1933	Soviet Union scientists observed stimulating effect of La on wheat growth, but an inhibiting effect of Ce.	Savostin and Terner (1937) and Dorobkov (1941)
1960	Romanian and Bulgarian scientists reported 24% yield increase of wheat after $CeCl_3$ application. They suspect improvements of photosynthesis as the reason.	Horovitz (1974) and Evanova (1964)
1972	Beginning of systematic research and application of REEs in Chinese agriculture.	Guo et al. (1988)
1979	First report on application of REEs in the USA.	Guo et al. (1988)
1980	Japanese patent granted for the application of REEs to prevent soft-rotten disease in cabbage.	Kawasaki (1980)
1983	First report on application of REEs in the UK.	Andrew (1983)
1984	In China, 0.37 millions ha land were treated with REEs in field experiments testing a fertilizer called NONGLE.	Guo (1985)
1986	First commercial REEs fertilizer (CHANGLE-REEs) in China.	Guo et al. (1988) and Guo (1986)
1998	In China, 2.67 million ha commercially cropped land were treated with REEs. More than 100 crop species were reported to respond to REEs with yield increases of 5 to 10%.	Xiong et al. (2000)
2001	Australian scientists suggested that crop response to La were more significant under water-limited conditions.	Meehan et al. (2001)
2001	China produced 75,000 tons REO*, equivalent to 90% of the world's total production. Agricultural use accounted for 1100 tons of REO in China.	Hedrick (2002)

* REO= REEs as oxide.

Characterization of REEs

REEs show similar chemical and physical properties and represent a geo-chemically coherent group. REEs occur in nature predominately in (3^+) valence, Ce, however, is found in a stable tetrapositive state (4^+), and Pr and Tb are known to form higher valence oxides. REEs show an affinity to oxygen, and are found at higher concentration in phosphorites as well as in argillaceous sediments (Kabata-Pendias and Pendias, 2001). In Table 2.2, some important characteristics of REEs are summarized.

Table 2.2a: Characterization of REEs (adapted from CMRW, 2005 and Evans, 1990)

REEs	Atomic number	Atomic mass	Melting point (° C)	Boiling point (° C)	Crystal structure	No. of Stable forms
Sc	21	44.9	1541	2836	Hexagonal	45
Y	39	88.9	1522	3338	Hexagonal	89
La	57	138.9	920	3469	Hexagonal	139
Ce	58	140.1	795	3257	Cubic	136, 138, 142
Pr	59	140.9	935	3127	Hexagonal	141
Nd	60	144.2	1010	3127	Hexagonal	142, 143, 145
Pm	61	145.0	Unknown	Unknown	Hexagonal	145
Sm	62	150.4	1072	1900	Rhombohedral	144,149 150, 154
Eu	63	151.9	822	1597	Cubic	151, 153
Gd	64	157.3	1311	3233	Hexagonal	154-158, 160
Tb	65	158.9	1360	3041	Hexagonal	159
Dy	66	162.5	1412	2562	Hexagonal	156, 160-164
Ho	67	164.9	1470	2720	Hexagonal	165
Er	68	167.3	1522	2510	Hexagonal	162-168, 170
Tm	69	168.9	1545	1727	Hexagonal	169
Yb	70	173.0	824	1466	Cubic	168, 170-174
Lu	71	174.9	1656	3315	Hexagonal	175

Table 2.2b: Characterization of REEs (adapted from CMRW, 2005 and Evans, 1990)

REEs	Density (g cm^{-3})	Color	Date of discovery	Discoverer	Original name	Use
Sc	2.99	Silvery	1879	Lars Nilson	Scandinavia	Ceramics, Laser, Crystals
Y	4.47	Silvery	1794	Gadolin	Ytterby (village)	Ceramics, Laser, Plastics
La	6.7	White	1839	Mosander	To lie hidden (Gr.)	Expensive camera lenses
Ce	6.77	Gray	1804	Berzelius & Hisinger	Ceres (asteroid)	Heat-resistant alloys
Pr	6.77	Unknown	1885	von Welsbach	Gr. (green twin)	Coloring glass & ceramics
Nd	7.01	Silvery	1885	von Welsbach	Gr. (new twin)	Coloring glass & ceramics & IR
Pm	7.22	Unknown	1945	Marinsky	Prometheus (Gr. God)	Unknown
Sm	7.54	Silvery	1879	Lecoq de Boisbaudran	Samarskite (mineral)	Magnets, alloys with Co
Eu	5.26	Silvery	1896	Eugène Demarcay	Europe	Color T.V
Gd	7.9	Silvery	1880	Marignac	Johan Gadolin	Magnetic
Tb	8.23	Silvery	1843	Mosander	Yettery	Color T.V
Dy	8.55	Unknown	1886	Lecoq de Boisbaudran	Gr. from dysprositos	Nuclear reactors
Ho	8.8	Silvery	1879	Cleve	Latin (holmia)	Nuclear reactors
Er	9.07	Gray	1843	Mosander	Yettery	Ceramics
Tm	9.32	Silvery	1878	Cleve	Thule	Power for portable X-ray's
Yb	6.97	Silvery	1878	Marignac	Ytterby	Metallurgical, chemical experiments
Lu	9.85	Silvery	1907	Urbain	Lutetia (Lt. of Paris)	Unknown

Table 2.2c: Characterization of REEs (adapted from CMRW, 2005 and Evans, 1990)

REEs	Common compound	Oxidation state (valence)	Electron configuration	Acid/base properties	Electro-negativity coefficient	Energy of vaporization ($KJ\ mol^{-1}$)
Sc	Sc_2O_3, ScH_2, ScH_3	3	$3d^1\ 4s^2$	Neutral	1.36	314.2
Y	Y_2O_3, YH_2, YH_3, YCl_3	3	$4d^1\ 5s^2$	Neutral	1.22	367.4
La	La_2O_3, $LaCl_3 \times 3H_2O$, $LaCl_3 \times 7H_2O$	3	$5d^1\ 6s^2$	Basic	1.10	339.57
Ce	Ce_2O_3, $CeCl_2$	3, 4	$4f^2\ 6s^2$	Basic	1.12	313.8
Pr	Pr_2O_3, $PrCl_3$	3	$4f^5\ 6s^2$	Basic	1.13	332.6
Nd	Nd_2O_3, $NdCl_3$	3	$4f^4\ 6s^2$	Basic	1.14	283.68
Pm	Pm_2O_3, $PmCl_3$	3	$4f^5\ 6s^2$	Basic	1.13	-
Sm	Sm_2O_3, $SmCl_3$	3,2	$4f^6\ 6s^2$	Basic	1.17	191.63
Eu	Eu_2O_3, $EuCl_3$	3,2	$4f^7\ 6s^2$	Basic	1.20	175.73
Gd	Gd_2O_3, $GdCl_3 \times 6H_2O$	3	$4f^7\ 5d^1\ 6s^2$	Basic	1.20	311.71
Tb	Tb_2O_3, $TbCl_3$	3,4	$4f^9\ 6s^2$	Basic	1.10	-
Dy	Dy_2O_3, $Dy\ Cl_3$	3	$4f^{10}\ 6s^2$	Basic	1.22	230
Ho	Ho_2O_3, $HoCl_3$	3	$4f^{11}\ 6s^2$	Basic	1.23	251.04
Er	Er_2O_3, $ErCl_3 \times 6\ H_2O$	3	$4f^{12}\ 6s^2$	Basic	1.24	292.88
Tm	Tm_2O_3, $TmCl_3 \times 7H_2O$	3	$4f^{13}\ 6s^2$	Basic	1.25	191
Yb	Yb_2O_3, $YbCl_3 \times 6H_2O$	3,2	$4f^{14}\ 6s^2$	Basic	1.10	128
Lu	Lu_2O_3, $LuCl_3$	3	$4f^{14}\ 5d^1\ 6s^2$	Basic	1.27	355

Table 2.2d: Characterization of REEs (adapted from CMRW, 2005 and Evans, 1990)

REEs	Energy of fusion ($KJ\ mol^{-1}$)	Electrical conductivity ($Ohm\ cm^{-1}$)	Thermal conductivity (W)	Ionic radius (Å)	Covalent radius (Å)	Mineral sources
Sc	14.10	0.017×10^6	15.8	0.75	1.61	Minerals (Thottveitile, wiikite)
Y	11.40	0.016×10^6	17.2	0.90	1.78	Monazite, xenotime, phosphates, carbonites
La	11.30	1.9×10^9	13.5	1.06	1.25	Monazite, bartnaesite
Ce	9.20	$1.4.\ 10^6$	11.4	1.03	1.65	Monazite
Pr	10.04	1.5×10^6	12.5	1.01	1.65	Salts
Nd	10.88	$1.6.\ 10^6$	16.5	0.99	1.64	Electrolysis of salts
Pm	-	2×10^6	17.9	0.98	1.63	Fission, products of U, thorium
Sm	11.09	1.1×10^6	13.3	0.96	1.62	Found with REEs
Eu	10.46	1.1×10^6	13.9	0.95	1.85	Man-made
Gd	15.48	0.8×10^6	10.6	0.94	1.61	Gadolinite
Tb	-	0.9×10^6	11.1	0.92	1.59	Found with REEs
Dy	11.06	1.1×10^6	10.7	0.91	1.59	Erbium, holmium
Ho	17.15	1.1×10^6	16.2	0.90	1.58	Gadolinite
Er	17.15	1.2×10^6	14.3	0.88	1.57	Heavy REE
Tm	16.80	1.3×10^6	16.8	0.87	1.56	Gadolinite, xenotime
Yb	7.70	3.7×10^6	34.9	0.86	1.70	Yttria, monazite, gadolinite
Lu	18.60	1.5×10^6	16.4	0.85	1.56	Gadolinite, xenotime

2.1 REEs in parent materials and soils

REEs in parent materials

REEs average abundance in the earth's crust varies from 66 µg g^{-1} in Ce, 40 µg g^{-1} in Nd and 35 µg g^{-1} in La to 0.5 µg g^{-1} in Tm, disregarding the extremely rare Pm (Table 2.3). Several of REEs are thus not very rare and occur widely dispersed in a variety of forms, especially as necessary minerals in granites, pegmatites, gneisses and related common types of rocks (Tyler, 2004).

Table 2.3: REE concentrations (µg g^{-1}) in the earth's crust, sea water, atmosphere and biosphere (adapted from Giungato and Notarnicola, 2003)

Material	Total REE concentration (µg g^{-1})	Material	Total REE concentration (µg g^{-1})
Earth's crust		**Sea water**	
Ocean basin rock	98	North Atlantic Ocean	14
Continental regions	237	Pacific Ocean	11
Carbonate rock	47		
Sediments and sedimentary rock	138		
Oceanic island volcanic rock	413		
		Biosphere	
Atmospheric particulate		Fowl and meat	0.07
Asian dust	145	Fruit	0.19
Catalyst reclamation particle	16194	Vegetables	0.23
Fluid catalyst cracker particles	8062	Grain	0.41
Oil- powered power plant particles	3008	Spinach	51
Coal- powered powder plant particles	975	Corn grain	5
Municipal incinerator particles	1.21	Corn leaves	122

The total content of REEs in soils varies according to the parent material in the following order: granite > quaternary > basalt > purple sandstone > red sandstone (Tables 2.4 and 2.5, Zhu and Liu, 1988). Soils developed from basic igneous rock, acid igneous rock, sandstone and shale rock usually have REEs values ranging from 174 to 219 µg g^{-1}, while soils originating from loess, and calcareous rock show lower REEs concentrations range from 137 to 174 µg g^{-1}. In soils from China the mean REEs content is 174 µg g^{-1}, while soil REEs content in Germany, Australia and Japan varies between 16 and 105 µg g^{-1} (Hu et al., 2006).

Table 2.4: Mean total REE content in soils from different types of parent materials (adapted from Liu, 1996)

Soil parent materials	Number of samples	Mean content (µg g^{-1})
Acid igneous rock	133	196
Neutral igneous rock	8	178
Basic igneous rock	5	216
Loess	70	174
Laterite	23	203
Sediment rock and shale	60	202
Sandstone	80	219
Lime rock	45	137
Purple sandstone	10	190
Sand-shale stone	21	174

Table 2.6 shows the concentration of REEs in some selected soils from different countries. REEs in soils are predominantly concentrated in minerals, such as fluorocarbonates, phosphates, silicates and oxides. The solubility of REEs in water derived from fluorocarbonates varies from $10^{-5} – 10^{-7}$ mol L^{-1}, that from hydroxides is approximately 10^{-6} mol L^{-1} and that from phosphates is in the range of $10^{-4} – 10^{-5}$ mol L^{-1}. Therefore, a limited amount of REEs occur in the water-soluble form in soils. This fraction can be directly taken up by plant roots and soil micro-organisms, or pass through the soil porous system. In 34 soils from China, the average water-soluble REE content was 0.27 µg g^{-1}, which accounted for 0.18% of the total REEs concentration (Hu et al., 2006).

Table 2.5: Content of REEs in different types of soils (µg g^{-1}) in China and some factors affecting it (Wang et al., 1998)

	Soil types					
	Red earth	**Latosol**	**Albic bleached soil**	**Leached chernozem**	**Yellow brow soil**	**Cinnamon soil**
Soil properties						
Soil depth (cm)	0-10	5-18	0-25	0-25	0-26	0-9
pH	4.18	4.30	5.62	5.95	6.90	7.80
Organic matter[a]	3.60	3.68	4.05	5.84	2.38	1.75
Fulvic/ humic	3.94	5.42	1.44	0.66	2.33	1.13
CEC[b]	10.7	11.6	18.49	34.8	22.3	14.4
Climatic zone	central subtropical	tropical	temperate	temperate	N subtropical Xiashu	warm temperate
Parent material	basalt	basalt	quaternary sediments	quaternary sediments	loess	loess
Total REEs[c]	86.3	251	229	186	229	192
La	14.3	46.9	53.5	38.8	46.7	37.6
Ce	29.6	75.9	88.9	76.2	102	77.9
Nd	21.1	72.9	44.9	36.2	38.7	39.0
Sm	3.25	10.6	7.06	5.94	7.25	5.82
Eu	0.75	3.34	1.45	1.29	1.29	1.30
Tb	0.40	1.37	0.93	0.71	0.81	0.82
Yb	2.33	2.28	2.65	2.47	3.05	2.92
Lu	0.418	0.397	0.465	0.417	0.475	0.431

[a] O.M, Organic Matter (%).
[b] CEC, cation exchange capacity, in. (10^{-2} me g^{-1} soil).
[c] Total REEs is sum of 15 REEs. The undetected elements were determined by interpolation in the relative abundance curves.

In China, the mean content of REEs in the soil is 174 µg g^{-1}. The REE content decreased from south to north. In the southern parts the REE content was higher than 200 µg g^{-1}, while in the northern parts this lower limit was never exceeded (Hu et al., 2006). In another study, Land et al. (1999) reported about total concentrations of REEs in the soil samples from Sweden from different horizons that the REEs have been fractionated during weathering. In the acidic E-horizon (pH 4.28), all REEs are depleted relative to the unweathered till. The depletion decreases with increasing atomic number. Also in the B-horizon (pH 5.86) the REE are depleted, although to a lesser extent compared to the E-horizon. Secondary phases in the B-horizon fractionate the REE in different ways. More studies were carried out in different countries e.g., in Japan (Yoshida et al., 1998), The Netherlands (Wang et al., 2000), Australia (Diatloff et al., 1996), Germany (Markert and Li, 1991; von Tucher and Schmidhalter, 2005), Egypt (Sharoubeem and Milad, 1966; Fakhry et al., 1989), USA (Wutscher and Perkins, 1993), Malaysia (Aidid, 1994), India (Ramakrishnan and Tiwari, 1998) on the variability of REEs in soils (Cited from Hu et al., 2006).

Table 2.6: Concentration ($\mu g\ g^{-1}$) of REEs in soils of some selected countries (adapted from Hu et al., 2006)

Element	Australia	Poland	Switzerland	Germany	Sweden	Japan	Malaysia	USA	China
La	15.4	13.0	17.8	3.5	17.7	18.2	30.5	13.6	37.5
Ce	60.5	25.7	36.1	5.9	29.0	39.8	52.8	25.7	77.3
Pr	4.1	2.4	-	0.9	7.2	4.5	-	2.4	7.8
Nd	14.6	9.9	15.0	2.5	13.5	17.6	28.7	9.9	29.3
Sm	2.8	1.4	2.8	0.5	3.0	3.6	4.8	1.4	5.7
Eu	0.8	0.3	0.5	0.1	0.7	0.9	0.9	0.3	1.1
Gd	2.6	2.8	-	0.5	2.5	3.7	21.1	2.8	5.1
Tb	0.4	0.1	0.3	0.1	0.6	0.5	1.3	0.1	0.8
Dy	2.1	0.7	-	0.5	2.5	3.2	4.9	0.7	4.6
Ho	0.2	0.2	-	0.1	0.5	0.6	-	0.2	0.9
Er	0.8	< 0.1	-	0.2	0.8	1.9	5.5	< 0.1	2.6
Tm	0.1	< 0.1	-	< 0.1	0.3	0.3	-	< 0.1	0.4
Yb	0.6	< 0.1	1.4	0.2	1.4	2.0	2.9	< 0.1	2.5
Lu	0.1	< 0.1	-	-	-	0.2	0.9	< 0.1	0.4
No. of samples	9	52	6	5	2	77	12	30	279
Total REEs	104.8	57.3	74.0	15.4	80.2	97.5	154.5	57.4	176.7

REEs in soils

REEs are a homogenous group of elements in the periodic system. They include the elements scandium, yttrium and 15 lanthanides with successive atomic numbers from 57 to 71. The lanthanides consist from lanthanum, to lutetium. In some classification schemes, the lanthanides are termed “rare earth elements”, which include the additional elements (Y) and (Sc), because these two metals and the lanthanides possess similar chemical and toxicological properties, and they occur together with the lanthanides in ores.

In fact, the term “rare earth elements” is misleading because these elements are not rare. The abundances of Ce (average concentration in the earth’s crust is 60 $\mu g\ g^{-1}$), La (30 $\mu g\ g^{-1}$), and Nd (28 $\mu g\ g^{-1}$) are similar to those of copper (55 $\mu g\ g^{-1}$), lead, tin and cobalt (Hedrick, 2000). Lutetium and Tm are the least abundant lanthanides at 0.5 $\mu g\ g^{-1}$, but exist at higher concentrations than antimony, bismuth, and cadmium (Goering, 2004). Hu et al. (2004) reported that the main content of REEs in the earth crust is approximately 0.015%, which matches that of copper, lead, zinc and is much higher than that of tin, cobalt, silver, and mercury. More than 250 kinds of minerals containing REEs are known. Only some of them (i.e. monazite, bastnaesite, xenotime, loparite, euxenite, and parisit) are important for industrial production for example metals, alloys, compounds, and fertilizers. The light REEs (La through Eu) are more abundant than heavy REEs (Gd through Lu), and furthermore, the elements with an even atomic number are more abundant than that with odd atomic numbers, because of the higher stability of their nuclei. REEs are never found as free metals in the earth and all their naturally occurring minerals are a mixture of various REEs and nonmetals (Zohravi, 2007).

Individual REE content in soils

Differences in the abundances of individual REEs in the upper continental crust of the earth represent the superposition of two effects, one nuclear and one geochemical. First, REEs with even atomic numbers (^{58}Ce, ^{60}Nd …) have greater cosmic and terrestrial abundances than adjacent REEs with odd atomic numbers (^{57}La, ^{59}Pr). Second, the lighter REEs are more incompatible (because they have larger ionic radii) and therefore more strongly concentrated in the continental crust than the heavier REEs. In most rare earth deposits, the first four REEs - La, Ce, Pr, and Nd - constitute 80 to 99% of the total content.

The results of soil analysis of 482 samples representing different soil types in China showed a mean La, Ce, Nd, Sm, and Eu content of 41, 74, 7, 28, and 6 µg g^{-1}, respectively (Hu et al., 2006). These five light REEs accounted for 90% of the total REE content. In comparison, the La, Ce, Nd, Sm, and Eu content in the earth crust is about 39, 60, 8.2, 28, and 6 µg g^{-1}, respectively (Vinogradov, 1959). These results reveal that the La and Ce content in Chinese soils is higher than that in the earth's crust. Basically, the concentration of individual REEs depends on the parent material and soil type. Soils derived from granite-gneiss and quartz-mica rock tend to contain higher concentrations of REEs (Ure and Bacon, 1978). On an average calcareous rock soils have the highest concentration of individual REEs. Paddy soils contain the highest concentration of light REEs, and latosol soils show the narrowest ratio of light to heavy REEs (Hu et al., 2006).

Distribution patterns of individual REEs in soils

The distribution of individual REEs in different binding forms shows a high variation in dependence on the soil type (Zhu and Xing, 1992a). Generally, higher concentrations of water soluble and exchangeable elements are found for those with an odd atomic number. In case of other binding forms, the differences proved to be minor (Zhu and Xing, 1992b). The share of individual REEs of the total REEs concentration varied highly, but decreased generally in the following order: Ce > La > Nd > Pr > Sm > Gd > Dy > Er > Tb > Ho > Tm > Lu (Hu et al., 2006).

Xiong et al. (2000) studied the plant availability of REEs in Chinese soils and found that the content of these elements ranged from traces below the detection limit values up to 208 µg g^{-1} with a mean value of 11.78 µg g^{-1} (the number of the total samples was 1790). The plant available REE content in acid soils was usually higher than that in calcareous soils (Xiong et al., 2000). The lowest plant available REEs content was found in black soils (Haplic Phaeozems), chernozem (Haplic chernozem), dark brown soils (Eutric Cambisol), gray sand soils (Cumulic-calcaric Regosol), and Shajiang soils (Gleyic Cambisol). Red soils (Ferralic Cambisol) proved to have the highest plant available REE content (18.8 µg g^{-1}) besides paddy soils (Hydrgric Anthrosols) (17.1 µg g^{-1}) (Xiong et al., 2000). There was a significant negative correlation between soil pH and the plant available REEs content in the range from pH 6 to 10 (Xiong et al., 2000).

Factors affecting mobility and bioavailability of REEs in soils

In recent years, more and more REEs entered the environment through various pathways because of the rapid increase of the exploitation of REE resources and its applications in modern industry, agriculture and everyday life. Many efforts have been made to understand the chemical behavior and bioavailability of REEs in the environment (Wyttenbach et al., 1998; Li et al., 1998a; Zhang and Shan, 2001; Lu et al., 2003). It is well established that the physico-chemical properties of soils (e.g. organic matter content, pH, and CEC) are the main factors controlling the mobility, transformation, and bioavailability of REEs in soils (Figure 2.1, Shan et al., 2004). The chemical fractionations of REEs afford valuable information in evaluating the bioavailability of these elements in soils (cited from Wen et al., 2006).

It was observed that soil pH, concentration levels of ions, and other chemical properties of soil were affected by plant roots during plant growth stages. For example, when plant roots adsorb nutrient cations, the roots may release H^+ to maintain their electrical neutrality. Soil pH near roots may, therefore, differ considerably from that a few millimeters away. The phenomenon should affect the mobility and the bioavailability of REEs in the soil environment, because soil pH affects REE dissolution (Figure 2.1, Nakamaru et al., 2006).

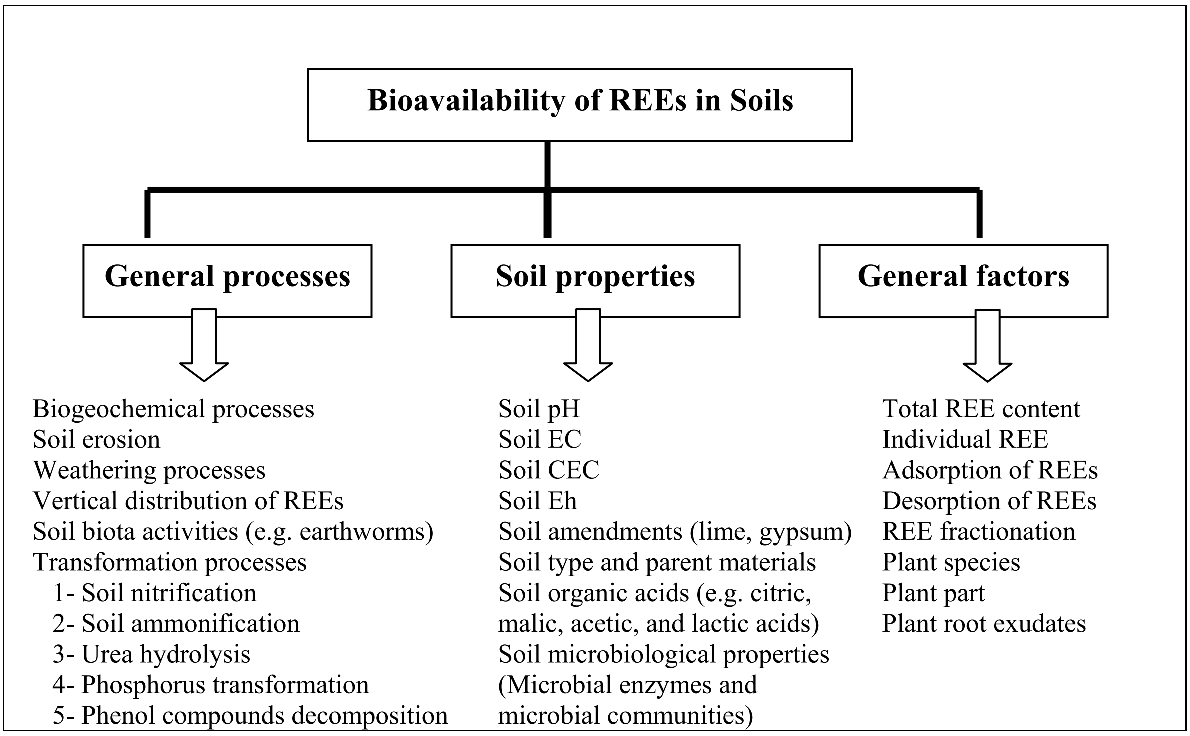


Figure 2.1: Factors affecting the bioavailability of REEs in soils

Migration of REEs in soils

Translocation and leaching of REEs in soils may result in groundwater contamination and dispersion of REEs in the environment. Leaching of the radioactive labeled isotopes, ^{141}Ce and ^{147}Nd, in columns was analyzed using nine different types of soils from China (Zhang et al., 1995). In this experiment, ^{141}Ce and ^{147}Nd solutions was added on top of the soil columns at rates of 25% and 50% of the maximum REEs adsorption. The soil columns were leached with distilled water and/or 0.01M $CaCl_2$ for 48-72 hours, stimulating an annual rainfall of 600-1500 mm. Soil samples from different depths and leaches were analyzed. The elements ^{141}Ce and ^{147}Nd were translocated into a depth of 6-10 cm and 4 cm, respectively in acid soils. In other soil column studies added REEs were found in the topsoil layers of 0-5 cm (Stocks et al., 2001). These experiments showed that the risk of ground water pollution by REEs through leaching seems low (cited from Hu et al., 2006).

Some groundwater and plants were contaminated by high amount of REEs in some ion-type REEs mineral zones and in long-term-application sewage sludge soils (Essington and Mattigod, 1990; Zhu et al., 1995). To some extent, the content of REEs in plants and groundwater depends upon the REEs contents in soil and the reactions at soil–water interface. REEs in soil can move into soil solution. This solution may be transported to adjoining surface and groundwater, thereby affecting whole ecosystem. It is, thus, significant to investigate the REE release from soils (Cao et al., 2001).

A few researchers (Ran and Liu, 1993a; Chang and Zhu, 1996) reported that the adsorption–desorption behavior of REEs on the soil surface. Whereas, some work has been conducted to determine the bioavailability, speciation and transport of REEs in the soil–plant system (Cao et al., 2000). Under natural conditions, an annual translocation rate by precipitation of about 1 cm was determined, when REEs were applied in rates equivalent to 10% of the adsorption saturation on acids soils with a low adsorption capacity, of about 0.5 cm on slightly acid soils with a moderate adsorption capacity. No translocation of REEs was found on alkaline soils with high adsorption capacity (Zhu et al., 1996). The main factors influencing the translocation rate are soil pH for the HAc extractable REEs, and Fe-Mn-oxides for HCl and HNO_3 extractable REEs (cited from Hu et al., 2006).

Soil pH and Redox Potential (Eh)

Equilibrium release experiments were conducted under three different pH values of 3.5, 5.5 and 7.5 as well as three redox potentials of 400, 0 and – 100 Mv to investigate the influence of redox potential and pH value on the La, Ce, Gd and Y release of from the simulated-REEs-accumulation soil. Results indicated that La, Ce, Gd, and Y release increased gradually with the decrease of pH value or Eh, and the influence of redox potential on Ce was more remarkable than on La, Gd and Y. Low pH and redox potential were more favorable to La, Ce, Gd and Y releases following the change of their species (Cao et al., 2001). The plant available REEs content in acid soils is usually higher than in calcareous soils. There is a significant negative correlation between soil pH and plant available REEs content in the range from soil pH 6 to 10. The plant available REEs content increases with increasing clay and organic matter content of soils (Xiong et al., 2000).

With decreasing redox potential, the soluble REEs contents increased with each Eh decrement. A decrease in soil pH and Eh was associated with an increasing availability of La, Ce, Gd and Y. Under reducing soil conditions and at low pH values, the dissolution of Fe-Mn oxyhydroxides released REEs. Hereby, the redox potential had a stronger influence on the release of Ce than La, Gd and Y. This phenomenon could be related to changes in the valences of Ce, Ce^{2+} and Ce^{4+} side by side with oxidation and reduction processes (Hu et al., 2006).

Addition of lime ($CaCO_3$) increased soil solution pH and decreased REE concentrations in soil solution, whilst gypsum ($CaSO_4 \times 2H_2O$) decreased soil solution pH and increased the concentrations of REEs in soil solution (Diatloff et al., 1996). In study about the effects of soil amendments on concentration of REEs in some Australian soils, Diatloff et al., (1996) found that the pH of the soil solutions extracted from 10 unamended acid soils (control) ranged from 3.9 to 4.9. The addition of $CaCO_3$ to these 10 soils increased the soil solution pH, whereas the addition of $CaSO_4 \times 2H_2O$ tended to decrease the pH of the extracted soil solution. The concentration of total REEs measured in the soil solution extracted from the 10 unamended acid soils (control) ranged from < 0.007 to 0.49 μM. The concentrations of total REEs in the soil solution of soils treated with $CaCO_3$ ranged from < 0.007 to 0.13 μM. The corresponding concentration of range in the soil solution of soils amended with $CaSO_4 \times 2H_2O$ was much higher (0.03 – 4.05 μM). Table 2.7 shows the effects of lime and gypsum on pH, EC and means REE concentrations in soil solutions extracted from 10 Australian acid soils expressed in mass units.

Table 2.7: Effects of amendment with $CaCO_3$ or $CaSO_4 \times 2H_2O$ on pH, EC (dS m^{-1}), and mean REE concentrations in soil solutions extracted from 10 Australian acid soils (adapted from Diatloff et al., 1996)

		Soil properties			REEs content (μg g^{-1})			
Soil location	**Soil Amendment**	**Site used (initial pH)**	**pH**	**EC**	**La**	**Ce**	**Nd**	**Y**
Condong	Control	Cultivated	4.1	0.18	0.001	0.003	0.003	0.002
	+ $CaCO_3$	(4.70)	6.8	0.40	0.001	0.001	0.001	0.002
	+ $CaSO_4 \times 2H_2O$		3.7	1.48	0.043	0.088	0.052	0.061
Yandina	Control	Cultivated	3.9	0.18	-	0.001	-	-
	+ $CaCO_3$	(4.77)	4.5	0.40	-	-	-	-
	+ $CaSO_4 \times 2H_2O$		3.8	0.29	0.001	0.001	0.001	0.001
Silkwood	Control	Virgin	4.5	0.49	0.013	0.029	0.013	0.004
	+ $CaCO_3$	(4.88)	6.8	0.65	0.004	0.007	0.004	0.001
	+ $CaSO_4 \times 2H_2O$		4.1	1.68	0.013	0.027	0.013	0.004
Julatten	Control	Virgin	3.9	0.13	-	-	-	-
	+ $CaCO_3$	(4.88)	6.9	0.28	-	-	-	-
	+ $CaSO_4 \times 2H_2O$		3.8	0.94	0.006	0.015	0.003	0.003
Cooloolabin	Control	Cultivated	4.0	0.50	0.001	0.004	0.003	0.001
	+ $CaCO_3$	(4.99)	6.0	0.53	0.013	0.003	0.001	-
	+ $CaSO_4 \times 2H_2O$		3.9	1.56	0.040	0.063	0.020	0.011
Jacobs Well	Control	Virgin	4.0	0.81	0.001	0.003	0.001	0.001
	+ $CaCO_3$	(5. 01)	4.8	0.94	0.001	0.004	0.003	0.002
	+ $CaSO_4 \times 2H_2O$		3.9	1.56	0.135	0.196	0.078	0.062
Jacobs Well	Control	Virgin	4.3	0.60	0.018	0.001	-	-
	+ $CaCO_3$	(5.32)	4.9	0.58	-	-	-	-
	+ $CaSO_4 \times 2H_2O$		4.1	2.58	0.001	0.001	0.001	-
Jacobs Well	Control	Virgin	4.3	0.29	0.001	0.001	0.001	-
	+ $CaCO_3$	(5.35)	5.1	0.32	0.001	0.001	-	-
	+ $CaSO_4 \times 2H_2O$		4.1	1.46	0.001	0.001	0.001	-
Yandina	Control	Virgin	4.9	0.29	0.001	0.001	0.001	0.001
	+ $CaCO_3$	(5.46)	6.4	0.32	-	0.001	0.001	-
	+ $CaSO_4 \times 2H_2O$		4.3	2.06	0.004	0.007	0.001	0.002
Bli Bli	Control	Cultivated	4.0	0.62	0.001	-	-	-
	+ $CaCO_3$	(5.46)	4.4	0.81	-	-	-	-
	+ $CaSO_4 \times 2H_2O$		3.8	1.86	0.004	0.006	0.004	0.001

Organic Acids

Complexation of REEs by organic and inorganic ligands plays a controlling role on their mobility, effective solubility, reactivity and chemical fractionation in the environment (Shan et al., 2002; Ding et al., 2005a). For example, it is suggested that carbonate complexes dominate REE complexations in the neutral to alkaline natural waters, whereas the free ions and sulfate complexes are the main species in acidic waters (Tang and Johannesson, 2003). A few studies have shown that the toxicity and bioavailability of REEs are mainly related to their free-ion forms (Cacheris et al., 1990; Stanley and Byrne, 1990; Wang et al., 2004; Weltje et al., 2004; Wen et al., 2006), implying the potential biological importance of REE complexation with dissolved ligands. Humic substances (HS) like humic acid (HA) and fulvic acid (FA) are the main organic ligands interacting with metal ions in natural aquifer. Studies using ultrafiltration suggest that REEs are closely associated with humic substances in many natural waters (Tanizaki et al., 1992; Viers et al., 1997; Ingri et al., 2000). Correspondingly, several analytical approaches have been employed to investigate the complexation of REEs with purified humic materials (Takahashi et al., 1997; Sonke and Salters, 2006; Ding et al., 2006a).

Recently, the effects of organic ligands on the bioaccumulation and bioavailability of REEs in soil-plant ecosystem and in aqueous system have been investigated, but less work has been done for the effects of organic matter in soil ecosystems. In natural soil system, organic ligands, such as organic acid, fulvic acid (FA), humic acid, plant root exudates, etc., play a very important role in altering the REEs bioavailability by complexing REEs in soil (Gu et al., 2001). Some work should be done to find a method that can reliably estimate bioavailability of REEs to plants and thereby evaluate the potential health risk of REEs in soils and predict their impact on the ecosystem (Xinde, 2000).

REEs and soil microbiological activity

Research on the effect of REEs on soil microorganisms and enzyme activity had been conducted before (Chu et al., 2001a; Chu et al., 2001b; Chu et al., 2003a). At low concentrations La had a slight stimulatory effect on soil bacteria and actinomycetes, whereas it inhibited soil bacteria, actinomycetes and fungi at high concentrations in pot experiment (Chu et al., 2001a). La stimulated nitrification in soil at lower concentrations, but inhibited it at higher concentrations (Zhu et al., 2002; Chen and Zhao, 2007).

There are some microorganisms, which accumulate specific elements such as iron (Fe) (Roden and Lovley, 1993), sulfur (S) (Sakaguchi et al., 1993) and uranium (U) (Macaskie et al., 1992). It is possible that microorganisms that can actively accumulate REEs may exist in nature but so far no proof exists. Furthermore, oligotrophic microorganisms have been shown to be highly capable in the uptake of nutrients and various inorganic elements to support their growth under poor nutritional conditions (Kamijo et al., 1999).

In the last 15 years, numerous studies have shown that micro-organisms (bacteria, yeast and fungi) may interact with ions such as heavy metals or radionucloides. Many types of phenomena can take place, such as biosorption, bioaccumulation, resistance/detoxification mechanisms and direct or indirect utilization in the microbial metabolism. Major advantages in the use of Biosorption materials are relatively low cost and good metal uptake capacities, which may in some cases, be even highly specific for a certain metal of particular interest. The lanthanide Biosorption equilibrium obeyed the Brunauer – Emmett – Teller isotherm model, indicating multilayer adsorption (Texier et al., 1999).

It has been shown that La, Eu and Tb were accumulated during growth, in the space between the inner and outer membrane of the cell envelope (periplasmic space) of *Escherichia coli* (Bayer and Bayer, 1991). The structural effect of REE ions on the bacterial cell is rapid and consists of the formation of periplasmic precipitates containing La and P. Tb appears to form small deposits at contact sites of outer and inner membrane. The reaction is dependent on membrane energization and can be blocked by an excess of Ca. Growth at low ionic concentration of the medium also prevents formation of the periplasmic precipitate. On the other hand, they may influence the environment by producing mineral acids chelating agents such as siderophores, or by-products of the metabolism (organic acids etc.). For example, the interactions between a mycobacterial siderophore (mycobactin) and Eu ions have been shown by a spectrophotometeric approach. Moreover, some siderophores such as ferrioxamine B could deplete Eu fixation by goethite or boehmite. Biosorption encompasses the uptake of metals by the whole biomass (living or dead) through physico-chemical mechanisms such as, ion exchange or surface precipitation. The processes take place on the cell wall with rapid kinetics (Table 2.8, Andrès et al., 2003).

Gram-positive bacteria, such as *Bacillus licheniformis* had a high ability to accumulate REEs. The abilities of various microorganisms to accumulate REEs from a solution containing one kind of REE were almost identical. However, tests with solutions containing two REEs showed that all of the gram-positive bacteria and actinomycetes could accumulate larger amounts Eu than Gd. Also, most of the actinomycetes removed more Eu than Sm. In a solution containing five REEs (Y, La, Sm, Er, and Lu), fungi *Mucor javanicus* preferentially Sm when *Streptomyces flaviridis* was used, Lu was preferentially accumulated. This means that it is possible to accumulate and separate REEs in selected microorganisms (Tsuruta, 2007).

Table 2.8: Comparison of maximum biosorption capacities of various micro-organisms for several rare earth metal ions from different authors (adapted from Andrès et al., 2003)

Micro-organism	Element	Biosorption (mg g^{-1} dw)	pH of medium
Pseudomonas aeruginosa (CIP A22)	La^{3+}	55.1	pH 5.0
	Eu^{3+}	44.1	pH 5.0
	Yb^{3+}	56.4	pH 5.0
	Gd^{3+}	50.6	pH 5.0
Pseudomonas putida (CCUG28920)	Eu^{3+}	50.2	pH 6.4, 0.01 MCl
Pseudomonas aeruginosa	La^{3+}	20.0	pH 4.0, 10 mMCa(NO_3)$_2$
Pseudomonas aeruginosa (MTCC-1223)	La^{3+}	139.0	pH 5.0 acetate buffer
	Pr^{3+}	132.5	pH 5.0 acetate buffer
	Nd^{3+}	158.4	pH 5.0 acetate buffer
	Eu^{3+}	126.2	pH 5.0 acetate buffer
	Dy^{3+}	163.0	pH 5.0 acetate buffer
Bacillus cereus	La^{3+}	4.6	pH 4.0, 10mM Ca(NO_3)$_2$
Bacillus subtilis	La^{3+}	15.8	pH 4.0, 10mM Ca(NO_3)$_2$
Bacillus subtilis (CIP 5265)	Gd^{3+}	54.9	pH 5.0
Myxococcus xanthus	La^{3+}	90.4	pH 4.5
Mycobacterium smegmatis (CIP 7326)	Yb^{3+}	17.8	pH 1.5
	La^{3+}	7.9	pH 1.5
	Eu^{3+}	15.4	pH 1.5
	Gd^{3+}	17.3	pH 5.0
Ralstonia metalidurans CH34 (*Alcaligenes eutrophus* CH34)	Gd^{3+}	23.1	pH 5.0
Escherichia coli	La^{3+}	9.7	pH 4.0, 10mM Ca(NO_3)$_2$
Saccharomyces cerevisiae	Gd^{3+}	0.8	pH 5.0
Saccharomyces cerevisiae (Brewery strain)	La^{3+}	77.8	pH 4.5
Saccharomyces cerevisiae	Sc^{3+}	6.0	pH 0.6
Candida valida	Sc^{3+}	4.5	pH 0.6
Rhizopus arrhizus	La^{3+}	48.7	pH 3.5 – 4.0
Rhizopus arrhizus	Sc^{3+}	16.5	pH 0.6
Brewer's yeast waste	La^{3+}	90.4	pH 4.5 dry at 100 °C, sieved 50-60 mesh
Asperigillus niger	Sc^{3+}	2.3	pH 0.6
Asperigillus terreus	Sc^{3+}	6.9	pH 0.6
Shewanella putrefaciens (CCUG-22948)	Pm^{3+}	0.3	pH 4.0

Toxicology of REEs on soil microorganisms

Toxic effects of heavy metals on soil microorganisms have been extensively studied in the past, and almost every group of organisms has been studied in this respect (van Beelen and Doelman 1997; Giller et al., 1998). Fungi and bacteria constitute the main components of the soil microbial biomass. It has often been stated that fungi are more tolerant of heavy metals than bacteria (Frostegård and Bååth, 1996). This was initially inferred by comparison of metal tolerance of pure culture isolates of soil microorganism (Babich and Stotzky, 1978). To compare heavy metal effects on the saprotrophic part of the fungal and bacterial communities, experiments should be performed without the involvement of plants. Furthermore, measurements of activity would be the most direct way of comparing these two groups of microorganisms, since this is a more sensitive measure than biomass measurements

(Rajapaksha et al., 2004).

The influence of toxicants on microorganisms has often been studied under controlled conditions. The heavy metal effects on the soil microbial community have been investigated quantitatively (plate count, ATP and direct observation) or with emphasis on specific microbial activities (soil enzymes, N_2 fixation and respiration) as well as by estimating heavy metal tolerance or microbial diversity (Karaca et al., 2002).

Chinese researchers have reported beneficial effects of low doses of REEs on a wide range of crops growing in soils, for example, when applied as foliar sprays, seed treatments, or added to solid or liquid rooting media (Guo 1987; Xiong 1995; Xie et al., 2002). However, these beneficial effects have seldom been reported in other countries. In contrast, the REEs have been shown to be highly toxic to microorganisms (Chu et al. 2003b; Tang et al., 2004). The harmful effects of excessive REEs on soil microbial biomass (Chu et al., 2001b), N transformations (Xu and Wang 2001; Zhu et al., 2002), CO_2 evolution, and enzyme activities (Chu et al. 2003b; Xu et al., 2004) have been reported in several studies. Until now, however, the application of REEs to soil has not been limited in China, and therefore, there is growing concern about the adverse effects of the accumulation of REEs in soils (Chu et al., 2007).

Zhou et al. (2004) studied the effect of exogenous REEs on microbial characteristics in paddy soils. They added rated concentrations of $RECl_3. \times 6H_2O$ and found that exogenous REEs had slightly stimulative effects on microbial indices in paddy soils at low concentration in the early stage after adding REEs, while having inhibitory effects at high concentration. The inhibition was strengthened with increasing REE concentration and was weakened with increasing incubation time. Principal component analysis of the BIOLOG (BIOLOG® redox technology is used to characterize heterotrophic microbial communities, Fang et al., 2001) data indicates that microbial community structure have changed, carbon source consumption of microorganisms in paddy soil becomes much more rapid after 8 weeks, and under REEs, the change of microbial community structures is a long-term effect (Zhou et al., 2004). After REEs application to soil, the changing process of microbial biomass may break into three stages as follows (Zhou et al., 2004):

(1) In the first stage, namely the first 4 weeks, the changes were very significant. All microbial biomass of the used samples decreased after one week. The largest degree of descent was about 36.8%, when 2000 µg g^{-1} REE added. When, the concentration of REEs was lower than 500 µg g^{-1}, microbial biomass turns up an increasing in the second week. The climatic time and maximum of microbial biomass significantly differed under different concentrations. When the concentration was higher than 500 µg g^{-1}, microbial biomass

descended continuously.

(2) In the second stage, from 5th to 9th week, microbial biomass declined under different concentrations.

(3) In the third stage, after 7 weeks, the temporal availability of microbial biomass was not significant, while the concentration availability of microbial biomass was significant.

The populations of the three soil microbes (bacteria, actinomycetes and fungi) in a pure culture experiment decreased with the addition level of La ($LaCl_3$ levels were added into media at levels of 0, 25, 50, 100, 150, 200, 250 and 500 mg L^{-1}) (Chu et al., 2001a). This indicates that La was toxic to the soil microbes in pure culture, and the sensitivity of the three major microbial types to La was in a decreasing order actinomycetes > bacteria > fungi (Chu et al., 2001a). In comparison, in a pot experiment (levels of 0, 6, 30, 150, 300, 600 and 900 µg g^{-1} dry soil), La had a slightly stimulative effect on soil bacteria and actinomycetes when applied at low concentrations while had inhibitory effect on soil bacteria actinomycetes and fungi at high concentrations (Chu et al., 2001a). Chu et al. (2001b) found that the application of 100 mg La kg^{-1} dry soil significantly decreased the amounts of microbial biomass in red soil (China) under laboratory and greenhouse experiments.

Effects of REEs on enzyme activities in soil

Many experiments have been shown that effects of REEs on enzyme activities are diverse, the relation between REEs and enzymes activities is complex, and REEs can affect several kinds of enzyme activities (Xu et al., 2004). For example, under the effects of La and Ce, acid phosphatase activities of red soil (China) decreased continuously (Xu et al., 2004). In contrast, on yellow soil (China) the activities of acid phosphatase were stimulated mostly. The differences may associate with physical and chemical properties of the soil samples. The optimum pH value of soil acid phosphatase may be inhibited more significantly when the pH differences is bigger (Xu et al., 2004).

Soil enzymes catalyze reactions in soils that are important in cycling of nutrients such as C, N, P, and S. Accumulated enzymes are primarily of microbial origin but may also originate from plant and animal residue (Dick et al., 1994). Soil enzymes form a part of the soil matrix as exoenzymes and as endoenzymes in viable cells. Soil enzyme activities commonly correlate with microbial parameters. Microorganisms and plants synthesize enzymes, and in the soil they act as biological catalysts of important reactions to produce essential compounds for both soil microorganisms and plants. Assays of soil enzymatic activities include all of the enzymatic forms (biotic and abiotic) present in the soil (Nannipieri, 1994). They also determine the potential enzymatic activity of a soil under optimum conditions of moisture, pH, temperature and substrate concentration. Enzymatic activities may vary under stress, as when soil is contaminated by heavy metals (Dick, 1997). Soil enzymes are important for catalyzing innumerable reactions necessary for life processes of micro-organisms in soils, decomposition of organic residues, cycling of nutrients, and formation of organic matter and soil structure (Balota et al., 2004).

Soil enzymes are a kind of bioactive substances sensitive to environment. So, scientists suggested that enzymes might serve as indicators of evaluating the degree of heavy metal pollution in soil (Banerjee et al. 1997; Chu et al., 2002b). Many experiments have shown that effects of REEs on enzyme activities are broad, the relation between REEs and enzyme activities is complex and REEs can affect several kinds of enzyme activities (Chu et al., 2003a). For example: additions of La decreases the soil dehydrogenase activity and the recorded maximum decrease was 64% after 1 day of incubation with an application of 1000 mg La kg^{-1} dry soil. The inhibition of soil dehydrogenase activity La was gradually alleviated on prolonged incubation time (Chu et al., 2003a). They indicated that agricultural use of REEs such as La at excessive levels with produce harmful effects to soil microbial activity and microbially mediated soil function. Changes in soil dehydrogenase activity might be used as a sensitive indicator in assessing the level of REEs pollution in soil.

The activity of acid phosphatase in soil (pH= 4.1) declined the increasing of La and Ce concentrations up to 1000 µg g^{-1} dry soil. The maximum inhibitory ratio of La and Ce reached 69.8% and 71%, respectively. But La and Ce had stimulative effect on the activity of acid phosphatase in soil (pH= 5.2). Where, under effects of La and Ce, pH value of soil (4.1) decreased and then induced the decrease of acid phosphatase activity. On the contrary, pH value of soil (pH= 5.2) decreased and was closer to optimum pH (5.0). So, the activities of acid phosphates in soil (pH= 5.2) were stimulated (Xu et al., 2004). From the relationship between the enzyme activity and culture time, under effects of REEs of the same concentrations, soil acid phosphatase activities tended to increase with increasing of culture time. The explanations for this are that on one hand, increasing soil microorganisms lead to the increase of soil enzymes, on the other hand, the state and the amount of heavy metal existing in the soil led to the decrease of soil enzyme toxicity (Chu et al., 2000a).

Dehydrogenase activity

Dehydrogenase activity is considered as a suitable indicator of microbial activity because dehydrogenase only occurs within living cells, unlike other enzymes that can occur in the extracellular state. Brookes et al. (1984) reported that dehydrogenase activity was lower in metal-contaminated soil than in similar uncontaminated soil, whereas soil phosphatase activity was unaffected. Dehydrogenase activity is an intracellular process that occurs in every viable microbial cell and is measured to determine overall microbiological activity of soil. The problem with this is that the electron acceptors (2,3,5-triphenyltetraazolium chloride [TTC]) used in the assays are not very effective, and thus the measurements may underestimate the true dehydrogenase activity (Burns and Dick, 2002).

Additions of La decreased soil dehydrogenase activity and the recorded maximum decrease was 64% after 1 day of incubation with an application of 1000 mg La kg^{-1} dry soil. The inhibition of soil dehydrogenase activity by La was gradually alleviated on prolonged incubation time (Chu et al., 2003a). Their results indicated that agricultural use of REEs such as La at excessive levels would produce harmful effects to soil microbial activity and microbially mediated soil function. It is likely that change in soil dehydrogenase activity can be used as a sensitive indicator in assessing the level of REEs pollution in soil.

The inhibitory effects of La on soil CO_2 evolution were attributed to the direct toxicity of La with/without the indirect effect of decreased pH due to the addition of La. The inhibitory effects of La on soil dehydrogenase activity indicated that application of REEs could cause harmful effects on soil microbial activity and mediated soil function. Soil dehydrogenase activity may be a sensitive indicator in assessing environmental and ecological risks of REEs agricultural use in China (Chu et al., 2003a).

Phosphatase activity

Since the soil rhizosphere represents a complex of living communities, it is considered that soil alkaline phosphatase (AlP) and acid phosphatase (AcP) that are responsible for organic P transformation in soil, might be originating from extracellular and intracellular enzyme activities (Eichler et al., 2004). AcP activity in soil originates from many sources, including plant roots (Dinkelaker and Marschner, 1992), fungi (Tarafdar et al., 1988), mycorrhizal fungi (Tarafdar and Marschner, 1994) and bacteria (Tarafdar and Claassen, 1988). Soil microorganisms and soil fauna produce AlP, whereas higher plants are devoid of AlP (Tarafdar and Claassen, 1988). The activity of soil AlP and AcP that are responsible for hydrolysis of both esters and anhydrous H_3PO_4 of soil organic matter depends on various factors as soil type and its fertility, type of fertilization and nutrient management, soil microbiological activity, organic matter, soil pH, soil moisture and varieties of higher plant species. Roots and microorganisms release acid phosphatase, whereas microorganisms only produce alkaline phosphatase. Acid and alkaline phosphatase activities are often increased in the rhizosphere compared to the bulk soil (Tarafdar and Claassen, 1988).

Influence of REE fertilizer applications on soils characteristics

In the past 20 years, REEs turned out to be promising elements due to their excellent properties for fine chemistry modern industry. Therefore, environmental contamination from the widespread use of REEs is likely to increase. In addition, the intensive application of REEs in agriculture in the 80's in China requires a thorough investigation on their chemical behavior in the soil. The environmental behavior of REEs in soil is dominated by their low solubility. Fluorides, carbonates, phosphates and hydroxides may form complexes with neutral REEs with low solubility, resulting in low dissolved concentrations in the aqueous phase of ecosystem. In solution, REEs may be complexed with inorganic ligands (e.g. carbonate, sulfate), organic ligands (e.g., humic and fulvic acids) and at a high pH, with hydroxyl ions (Pan et al., 2002). In order to understand the behavior of REEs fertilizer and evaluate the bioavailability of REEs in soil further, a three-stage sequential extraction procedure was used to fractionate the exogenous REEs in soils. The behavior and bioavailability of REEs in soil associated with distinct geo-chemical phases is strongly dependent on the physicochemical properties of soil, such as soil particle size distribution, organic matter content, salinity, pH and redox potential.

Table 2.9 shows total content of REEs ($\mu g\ g^{-1}$) in some experimental sites in China with and without REEs fertilizer. Wang et al. (2003c) studied the effects of exogenous REEs fertilizer application on fraction of heavy metals in Chinese soils. Application of Fertilizer containing REEs may change the speciation distribution of heavy metals in soils. An increase in total extractable concentrations of heavy metals was detected in soils. In Addition to this, application of REEs fertilizer also changed the distribution of heavy metals in individual speciation fractions. After applying fertilizer containing REEs, a remarkable increase of REEs in elemental speciation fractions of soils was observed in Table 2.10.

Generally, the total content of REEs in soils ranges from 0.01% to 0.02%. Their concentrations in agricultural soils differ in relation to the type and usually vary between 76 and 629 $\mu g\ g^{-1}$ in China (Zeng et al., 2006). The speciation of REEs in the soil background was reported to include six forms, i.e., water-soluble form (0.05–0.17% in proportion), exchangeable form (0.02–6.5%), carbonate and specific adsorption form, Fe–Mn oxides form, organic-matter-bound form, and residual form (60–89%) (Zhu and Xing, 1992a). It is obvious that REEs exist mainly in residual form, which is unavailable to organisms. The percentage of the residual form varied greatly in different soils. For example, the percentage of residual form in red soil was 50–60%, while that in yellow brown soil was about 70% (Chen et al., 1995). The main bioavailable forms of La, such as soluble La and exchangeable La, contained in red soil were more than those in paddy soil by the same concentrations of La treatment (Xie et al., 2001).

Table 2.9: Total content of REEs in soils of experimental sites in China ($\mu g\ g^{-1}$) with and without REE fertilizer (adapted from Wen et al., 2001)

Element	Experimental site							
	Beijing [a]		Heilongjiang [b]		Jiangxi [c]		Anhui [d]	
	control	treated	control	treated	control	treated	control	treated
Y	12.4	12.5	9.11	10.23	1.53	2.99	1.87	4.48
La	29.8	29.8	17.59	19.64	4.63	10.38	4.36	16.82
Ce	62.7	62.1	35.14	35.39	7.47	1.39	7.99	30.29
Pr	7.21	7.38	4.36	4.31	0.78	1.84	1.01	3.13
Nd	27.5	26.9	15.74	16.13	2.74	7.23	4.33	6.59
Sm	4.98	4.88	3.39	3.41	0.46	1.06	1.66	1.51
Eu	1.11	1.23	0.67	0.76	0.09	0.27	0.13	0.35
Gd	5.27	5.17	3.18	2.99	0.59	1.18	0.63	1.35
Tb	0.68	0.79	0.36	0.46	0.07	0.15	0.20	0.20
Dy	4.07	4.97	2.56	2.57	0.48	1.17	0.65	0.68
Ho	0.76	0.78	0.48	0.46	0.08	0.19	0.12	0.20
Er	2.25	2.09	1.40	1.60	0.29	0.65	0.26	0.62
Tm	0.33	0.31	0.22	0.21	0.05	0.12	0.04	0.07
Yb	2.20	2.07	1.55	1.62	0.26	0.57	0.34	0.68
Lu	0.31	0.41	0.30	0.32	0.05	0.06	0.04	0.06

[a] The REEs fertilizer was applied at level of 165 g La ha^{-1}, 305 g Ce ha^{-1}
[b] The REEs fertilizer was applied at level of 165 g La ha^{-1}, 305 g Ce ha^{-1}
[c] The REEs fertilizer was applied at level of 2,260 g La ha^{-1}.
[d] The REEs fertilizer was applied at level of 1,130 g La ha^{-1}, 2,090 g Ce ha^{-1}

The behavior of REEs in soil is related to properties of this soil. Low pH values (Diatloff et al., 1996; Cao et al., 2001), but also lower cation-exchange capacity (CEC), organic-matter content (Jones 1997; Shan et al., 2002), and redox potential (Cao et al., 2001) all increase the solubility of REEs in soils. The addition of organic acids was found to decrease the adsorption of REEs to soil (Shan et al., 2002). Furthermore, the presence of REE-PO_4 (Johannesson et al., 1995; Diatloff et al., 1996) and metal-(hydr)oxides (Janssen and Verweij, 2003) are thought to play a role in the mobility of REEs. Therefore, it was concluded that, compared to their high availability in nutrient solution, the risk of toxic effects of REEs on plant growth is lower when REEs are added to soil. This is in line with the observation that humic and fulvic acids, which are commonly present in soil solution, may overcome the rhizotoxicity of La by complex formation (von Tucher and Schmidhalter, 2005).

Table 2.10: Concentrations of REEs as ranges and mean values in control and fertilized 15 Chinese soils compared with concentration of REEs in roots and shoots of wheat (adapted from Wang et al., 2003c)

	Range and mean values	Concentration of REEs ($\mu g\ g^{-1}$)			
		La	**Ce**	**Pr**	**Nd**
Shoots of wheat					
Control	Range	0.05 – 0.22	0.08 – 0.50	0.01 – 0.06	0.029 – 0.22
	Mean	0.11	0.19	0.02	0.06
Fertilized	Range	0.09 – 1.60	0.14 – 2.06	0.02 – 0.20	0.04 – 0.57
	Mean	0.36	0.51	0.05	0.15
Roots of wheat					
Control	Range	0.73 – 8.96	4.95 – 16.5	0.16 – 1.81	0.58 – 5.56
	Mean	4.30	11.3	1.03	3.52
Fertilized	Range	8.57 – 53.8	16.0 – 60.5	2.05 – 22.3	6.43 – 60.8
	Mean	25.1	45.1	6.00	17.20
Soil fractions					
B1 Control	Range	0.25 – 1.44	0.36 – 2.35	0.05 – 0.27	0.18 – 1.06
	Mean	0.53	0.87	0.10	0.38
Fertilized	Range	0.65 – 8.08	1.03 – 15.9	0.13 – 1.64	0.39 – 4.82
	Mean	1.71	2.93	0.32	1.02
B2 Control	Range	0.05 – 9.12	0.07 – 16.3	1.36	0.03 – 4.69
	Mean	3.11	6.17	0.52	1.74
Fertilized	Range	0.26 – 44.9	0.40 – 89.4	0.04 – 7.37	0.15 – 22.5
	Mean	8.05	13.8	1.21	3.76
B3 Control	Range	8.00 – 39.2	17.8 – 85.7	2.37 – 8.57	9.12 – 32.4
	Mean	20.6	50.5	5.30	20.1
Fertilized	Range	19.9 – 106	34.6 – 236	4.01 – 21.4	12.7 – 68.7
	Mean	48.2	108	10.8	36.9

B1= water soluble, exchangeable, carbonate bound form. B2= Fe- Mn oxide bound form.
B3 = organic and sulfide bound form. Total REEs fertilizer applied was 40 $\mu g\ g^{-1}$ soil.

It is generally accepted that the total REE content in soil is a poor indicator for the prediction of plant uptake. For the determination of plant availability in control (Li et al., 1998a) and REE-treated soils (Zhang and Shan, 2001), a sequential extraction procedure has been used. In both categories of soil, the REE content of rice, corn, and wheat were correlated significantly with the fraction of water-soluble, exchangeable, and carbonate-bound REE species that are extracted by 0.1 mol L^{-1} acetic acid. However, these correlations varied in different plant organs like roots, leaves, or grains. In addition, the uptake and content of REEs in plants differ considerably between plant species, even under natural conditions without supplementation (von Tucher and Schmidhalter, 2005).

The total REEs contents in Chinese soils varied between 68 and 629 $\mu g\ g^{-1}$, with a mean concentration of 181 $\mu g\ g^{-1}$ (Hu et al., 2006). Total, exchangeable, and soil solution concentrations were measured for 15 REEs in nine Australian soils from Queensland and New South Wales (Diatloff et al., 1996). The exchangeable REEs was extracted using 0.1 M $Ca(NO_3)_2$ and *aqua regia* for the total REE content. The concentration of total exchangeable REEs in these Australian soils ranged from < 0.5 to 8.2 $\mu g\ g^{-1}$ (Diatloff et al., 1996). The concentration of total REEs in these soils varied from 31.8 to 193.6 $\mu g\ g^{-1}$. The total REEs measured in the soil solutions accounted for 0.0003–0.009% of the total REEs extracted from the soils by aqua regia. The total exchangeable REEs accounted for 0.17 – 12.6% of the total REEs measured in the soils and extracted by *aqua regia*. This indicates that most REEs found in soils are not adsorbed to the soil exchange complex, but are most probably present as components of soil minerals and/ or complex with organic matter (Hu et al., 2006).

Influence of REE fertilizer applications on adsorption and desorption in soils

Since 1990 REEs have been applied to production fields as microelement fertilizer due to their abilities to enhance yields and improve quality of crops in China (Evans, 1990). Inevitably, large amounts of REEs move into the ecosystem. REEs may accumulate in soils and crops, and thus enter the food chain. This may cause a serious environmental problem in China. Many publications deal with the content, distribution of REEs in soils and plants (Wyttenbach et al., 1998; Cao et al., 2001).

In China, the use of mixtures of REEs in agriculture is widespread and aims at increasing growth of plants and animals. Commercially available mixtures are prepared from mineral ores and consist of all REEs with a predominant proportion of La and Ce (Brown et al., 1990; Xu et al., 2002). Results of positive effects of these additives on crop production are almost exclusively reported in Chinese literature. The enhancement of biomass production is reported to range between 8% and 50%, with an average yield increase of 8% - 15% (Brown et al., 1990; Hu et al., 2004). In addition, REEs are claimed to improve the nutritional quality and to be effective predominantly under stress conditions. However, results about the influence of REEs on plant development are contradictory. Beneficial effects may be restricted to certain growth stages (von Tucher and Schmidhalter, 2005).

Application of REEs in agriculture has been carried out intensively since 1972, aiming at increasing crop yields (Brown et al., 1990; Xiong, 1995). With this regard, much research work has been done to show the beneficial effects of REEs on plant growth and soil properties. For example, REEs were found to improve the bioavailability of calcium and manganese in soil (Chang, 1991), to stimulate the synthesis of chlorophyll (Guo, 1988), to promote seedling development (Chang, 1991; Wu et al., 1983), and to stimulate root and shoot growth in crops such as wheat (*Triticum aestivum* L.), cucumber (*Cucumis sativus* L.), soybean (*Glycine max* L. Merr.), and corn (Wu et al., 1983, 1984). Much less work has been done on possible adverse effects of REEs (Cited from Wang et al., 2001c).

The chemical speciation of soil amended REEs is linked to the soil type. REEs applied to many types of soils, e.g. Latosol (Rhodic Ferralsol), yellow brown earth (Haplic Luvisol), black soil (Haplic Phaeozems), and Chernozem (Haplic Chernozems) and REEs which applied to these soils were mainly found in amorphous Fe-Mn-oxides, and bound to organic matter. For example, REEs applied to a red earth soil (Ferralic Cambisol) that was low in pH and low in amorphous Fe-Mn-oxides were adsorbed and bound to Mn-oxides (Ran and Liu, 1993b). Only a low amount of adsorbed REEs in the inert form was found on Chernozems (Haplic Chenrozems), yellow-brown soils (Haplic Luvisol), lactosols (Rhodic Ferralsol) and red soils (Ferralic Cambisol), indicating that only a small portion of adsorbed REE ions was transferred into the mineral lattice (Ran and Liu, 1993b). In contrast, a relatively high amount of adsorbed REEs was found in the inert form on losses soils and dark brown soils (Eutric Cambisol) because of their higher pH values. The distribution coefficient (percent of certain REEs form increment in added REEs) of REEs added t a red soil (Ferralic Cambisol) and a yellow-brown soil (Haplic Luvisol) decreased in the following order: residual-REE > exchangeable REEs > organic matter bounded REEs > Fe/Mn oxide bounded REEs (Chen et al., 1995). In field experiments in China, all soil amended REEs were present in the water soluble, exchangeable, carbonate-bound, Fe-Mn-oxide bound, organic matter and sulfide bound form with variations of 1.5-13.9%, 35.2-70.3%, 19.1-60.8% of the total applied REEs rate (Wen et al., 2001). Generally, REEs applied to soils are transformed quickly (Liu et al., 1999; Hu et al., 2006).

The REEs in generally used as fertilizers can increase crop production (Guo, 1988). Since the early 1980s the amount of REEs used in agriculture increased, reaching a few thousand tons each year and was applied over more than three million hectare up to 1998 in China (Guo, 1999). The fate of REEs used in agriculture has become a growing concern after large quantities of REEs accumulated in soil (Wang, 1991). It is very important, how REEs will be fixed and released and how the fixing and releasing rates will be used to study the bioavailability of REEs. It is generally accepted that metal concentrations in soil solution are most likely controlled by adsorption–desorption in soils. Therefore, the study on adsorption and desorption of REEs is very important. A lot of studies on the effect of soil mineral constituents and environmental conditions on the isotherm adsorption and desorption of exogenous REEs in soils have been done during past 10 years (Ran and Liu, 1993b; Chang and Zhu, 1996; Zhang et al. 1996). However, there are few reports that examined desorption, and even lesser reports that have measured desorption kinetics of REEs (cited from Li et al., 2001).

It is well established that the bioavailability, and potential toxicity or deficiency of trace metal ions in soils depend on their concentrations in the soil solution and on the soil's ability to release trace metal ions from the soil phase to replenish those removed from solutions by plants (Backes et al., 1995). The concentrations of metals in soil solutions are most likely to be controlled by sorption–desorption reactions (Hogg et al., 1993). From this point of view, study on the sorption–desorption reactions of REEs is important. Jones (1997) reported that adsorption of La, Y, Pr and Gd depended on soil pH and cation exchange capacity (CEC). The adsorption appeared to conform well to the single Langmuir equation. Equilibrium release experiments (Cao et al., 2001) demonstrated that the release of La, Ce, Gd and Y increased with decreasing pH or Eh. It was also reported that the release of REEs were correlated with the release of Fe and Mn, suggesting that the release of REEs originated from dissolution of Fe–Mn oxyhydroxides under the reduced and low soil pH conditions (Li et al., 1998a). The adsorption of REEs increased with increasing soil pH (Ran and Liu, 1992; Ran and Liu, 1993a). Li et al. (2001) studied the kinetics of adsorption and desorption of Ce(III) on soil using a batch method and isotope ^{141}Ce. It was indicated that the Elovich equation proved to fit the data on desorption of Ce(III) from fluvoaquic and black soils well, while the parabolic-diffusion equation were the best models for red earth and loess soils (Shan et al., 2002).

In six soil samples of different soil types taken in China, > 95% of the added REEs were adsorbed (Zhu et al., 1993) to oxides of clay minerals and organic matter (Beckwith and Butler, 1993). The soil clay fraction (< 2 μm) consists of clay minerals such as illite, kaolinite, smectite, etc., and hydrous metal oxides, for example Fe, Mn and Al. The Fe and Mn oxides can co-precipitate and adsorb cations from the solution due to their pH-dependent charge (Alloway, 1995). It has been suggested that these metal oxides are primarily responsible for accumulating REEs in soils (Peng and Wang, 1996). Organic matter contributes significantly to the adsorption of REEs due to the dissociation of protons from carboxyl and phenolic groups of humic polymers in the soil (Beckwith and Butler, 1993). The soil pH value is another important factor influencing the adsorption of REEs (Wang et al., 2001). The adsorption of REEs generally increased with increasing soil pH values, because the surface of soil particles is charged with more OH^- ions, so that dissolved REEs ions can easily form complexes, such as $Ln(OH)^{2+}$, $Ln(OH)^-_4$ (Zhu et al., 1993; Hu et al., 2006).

Zhu et al. (1993) studied the adsorption and desorption of exogenous REEs in soils. They found that the adsorption rate of REEs is also affected by the concentration of electrolyte, since their existed exchange reactions among the cations in the solution and the REEs ions sorbed by the soil samples. The high concentration of electrolytes lead to replacement of REEs ions sorbed. The adsorption of REEs is much higher in soils of higher pH. When the pH value of soils is high, the surface of soil particles possess more OH^{-1} ions, and consequently REEs ions in solution could easily form complex ions and are considered to be more strongly adsorbed at the sites covered with OH^{-1}. In the case of lower pH, competition between REEs ions and H^+ might cause a lower rate of adsorption, being the reason why adsorption of REEs increased with increasing pH.

Pang et al. (2002) reported about the adsorption and desorption of REEs in soil and minerals (Table 2.11). Other studies have shown that the environmental behaviors of REEs in soil are dominated by their low solubility (Weltje, 1997). Fluorides, carbonates, phosphates and hydroxides may form neutral complexes containing REEs with a low solubility. The amount of exogenous REEs demonstrates the following relationship: residual >> bound to organic matter > bound to Fe-Mn oxides > bound to carbonate >> exchangeable and water soluble forms. The adsorption capacity of REEs depends on the clay type and the content of amorphous and manganese oxides, the latter having the high adsorption ability. In contrast, the desorption of REEs is generally very low, with the exception of REEs being adsorbed by red soil and yellow brown soil (Peng and Wang, 1996).

Table 2.11: Desorption of adsorbed REEs by soils and minerals (adapted from Pang et al., 2002)

Samples	Adsorption (A) µg g^{-1}	Desorption (B) µg g^{-1}	Net (A-B)	Ratio of B/A	Maximum capacity of REEs adsorption (mg g^{-1})
Amorphous Fe oxides	6275 - 6625	Traces - 4.25	6275 - 6621	1	7.7
δ-MnO_2	5250 - 31500	Traces	5250 -31500	Traces	57.0
Kaolinite	344 - 850	222 - 740	106 - 122	64-87	0.9
Laterite	422 - 1525	81 - 798	341 - 727	19-52	1.6
Red soil	731	650	81	89	1.9
Yellow brown soil	1030	900	121	90	5.1
Black soil	1043	10	1033	1	12.7
Chernozem	1041-6238	11-2078	1030-4160	1-33	7.9

Information about desorption processes of REEs in soils is important with view to their plant availability, translocation processes and potential entry into the food chain. Basically, desorption is proportional to adsorption in soils. The adsorption of REEs to clay minerals and Fe/Mn-oxides is high while, the desorption is very low due to their strong specific binding. Desorption of REEs is also related to the soil pH. REEs desorption decreases from 90% to 29.5% when the soil pH increases from 4.1 to 6.3. REEs desorb easily in the presence of organic acids like citric, malic, tartaric and acetic acid, to form complexes with these organic acids so that the adsorption will decrease of REEs, while was desorption processes increase. The organic ligand EDTA promoted desorption of REEs, which was proportional to its concentration (Hu et al., 2006).

Li et al. (2001) used low concentration REEs (20, 40 and 80 µg Ce mL^{-1}) as micro-fertilizer to study the kinetics of Ce(III) adsorption–desorption on four typical soils in China using the batch method with the radioactive nuclide ^{141}Ce. The used soils were fluvo-aquic soil from north of China; Red earth from Jiangxi Province, south of China; Black soil from Heilongjiang Province, northeast of China; and Loess soil from Shaanxi Province, southwest of China. Results indicated that Ce(III) adsorption was rapid and nearly finished in less than 0.5 min. Desorption procedure was about completed in 1–30 min in the tested soils. Ce(III) desorption equilibrium times vary with different soils. The decreasing order of Ce(III) desorption equilibrium time was red earth > fluvo-aquic soil > black soil > loess soil; and the decreasing order of Ce(III) desorption amount is red earth ≫ fluvo-aquic soil > loess soil > black soil. CEC of soil was significantly and negatively correlated to Ce(III) desorption equilibrium times and desorption amounts. The desorption of Ce(III) in the four types soils was controlled by the diffusion processes. The amounts of Ce(III) desorption on different soils in the same time were different. The Elovich equation proved to be the best models for fitting the data of Ce(III) desorption reactions in fluvo-aquic soil and black soil; and the parabolic-diffusion equation was the best model in red earth and loess soil.

Desorption of REEs (as mentioned before) is also related to the soil pH. REE desorption decreases from 90% to 29.5% when the soil pH increases from 4.1 to 6.3 (Ran and Liu, 1992). Similar results were reported by Wen et al. (2002), who found that on an acid soil a pH of 5.4 and an organic matter content of 1.5%, the relative desorption of La (89.9 - 98.5%) and Ce (57.6 - 96.4%) were high. In contrast, on calcareous soils with high soil pH values between 7.2 and 8.2 and an organic matter of 36.4%, the relative desorption of La (27.6 -53.6%) and Ce (1.09 – 50.8%) were low (cited from Hu et al., 2006).

2.2 REEs in Plants

Contents of REEs in plants have been measured mostly using instrumental neutron activation analysis (INAA) (Ni et al., 1999; Wang et al., 1997). However, the INAA technique can only measure eight REEs (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) in plant samples. In recent years, high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) has been used to effectively measure the contents of individual REEs in biological and environmental samples. This highly sensitive and dissociative technique will further promote the study on the behaviors of individual REEs in biological samples (Xu et al., 2003a).

Table 2.12: Average concentrations of REEs in some plant species and the used soil

Plant species	REE concentration	REE content in soil	Reference
Pokeweed leaves (*Phytolacca americana*) **Fern leaves** (*Athyrium yokoscence*)	1.8 µg g^{-1} dw 622 µg g^{-1} dw 202 µg g^{-1} dw	Sandstone (76.5 µg g^{-1}) Andesite[a] (507 µg g^{-1}) -	Ichihashi et al. (1992)
Corn (*Zea mays* L.) Roots Leaves Stems Leaves Stems Roots Grains Flowers	 78.70 µg g^{-1}dw 0.16 µg g^{-1}dw 12.10 µg g^{-1}dw 4.70 µg g^{-1}dw 0.45 µg g^{-1}dw 15.40 µg g^{-1}dw 0.43 µg g^{-1} dw 2.30 µg g^{-1} dw	 Pot experiment[b] Luvisol[c] (275 µg g^{-1}) Plot experiment[d] (150 µg g^{-1})	 Wang et al. (2001a)
Oilseed rape (*Brassica juncea*) dry leaves	 53.4 µg g^{-1} dw	 228 µg g^{-1}	 Zhang et al. (2000)
Cabbage **Cabbage** (*Brassica oleracea*) **Chinese cabbage** (*B. pekinensis*)	0.15 – 2.6 µg kg^{-1} fw[e] 0.457 µg g^{-1} dw 1.474 µg g^{-1} dw	- 162 µg g^{-1} (Beijing)	Bibak et al. (1999) Wen et al. (2001)
Sprouts[f]	0.005-0.06 µg kg^{-1} fw	-	Bibak et al. (1999)
Wheat (*Triticum aestivum*) Roots Stems and leaves **Wheat** (*Triticum aestivum*) Roots Stems Leaves Grains	 La 0.009 µg g^{-1} dw La (0.006), Gd (0.002), Y(0.002) dw 3.91 µg g^{-1} dw 0.354 µg g^{-1} dw 1.84 µg g^{-1} dw 0.357 µg g^{-1} dw	- 162 µg g^{-1} (Beijing)	 Gu et al. (2001) Wen et al. (2001)
Vaccinium (*Vaccinium vitis-idaea*) Leaves (1)[g] Leaves (2)[h] Leaves (3)[i] **Pine** (*Pinus sylvestris*) Needles (1)[j] Needles (2)[k] **Pine** (needles) **Mosses** (*Sphagnum sp.*)	 1.62 µg g^{-1} dw 0.86 µg g^{-1} dw 0.54 µg g^{-1} dw 0.96 µg g^{-1} dw 1.08 µg g^{-1} dw 1.60 µg g^{-1}dw 2.94 µg g^{-1}dw	 5.6 µg g^{-1} 155 µg g^{-1} 22.5µg g^{-1} 22.5 µg g^{-1} 7.4 µg g^{-1} 171 µg g^{-1} (Osnabrueck, Germany)	 Markert (1987) Markert and Li (1991)
Citrus (leaves) **Tomato** (leaves) **Rye grass**	1.16 µg g^{-1}dw 4.69 µg g^{-1}dw 1.03 µg g^{-1}dw	171 µg g^{-1} (Osnabrueck, Germany)	Markert and Li (1991)
Cucumber (*Cucumis sativus*) **Tomato** (*L. esculentum*)	0.124 µg g^{-1} dw 0.053 µg g^{-1} dw	162 µg g^{-1} (Beijing)	Wen et al. (2001)
Rice (*Oryza sativa*) Roots Stems Leaves	 3.71 µg g^{-1} dw 0.185 µg g^{-1} dw 0.194 µg g^{-1} dw	 162 µg g^{-1} (Beijing)	Wen et al. (2001)

[a] Parent material, REEs = 155.6 µg g^{-1} dry weight.
[b] Applied concentration of REEs fertilizer was 20 µg REEs g^{-1} soil.
[c] REEs = sum of La, Ce, Pr, Nd, Sm, Gd, and Dy and the content of REEs in the fertilizer was 268 g kg^{-1}.
[d] Applied concentration of REEs fertilizer was 64 mg REEs m^{-2} soil and the sample was took at harvest (57 days after application).
[e] Fresh weight (fw) and the summation of REEs are for only La, Ce, Pr, Nd, and Gd.
[f] Fresh weight and the summation of REEs are for only Sm, Tb, Dy, Ho, Er, Tm, Yb, and Lu.
[g] Leaves (1), from soil location (10 Km south of Abisco, a peat bog called ‘Stordalen’)
[h] Leaves (2), from soil location (1 Km south of Abisco, north Sweden)
[i]. Leaves (3), from soil location (Achmer, 15 Km north Osnabrueck, Germany)

[j]. Needles (1), from soil location (Achmer, 15 Km north Osnabrueck, Germany)
[k]. Needles (2), from soil location (20 Km north east of Osnabrueck, a peat bog called ‘Venn Moor’)

Reports showed that the total REEs content of in plants ranged from 4 to 168 mg g^{-1}. The values were influenced by plant species and REE speciation in soils (Zeng et al., 2006). Table 2.12 shows this variation between some selected plant species. Concentrations of most elements in the aboveground biomass of vascular plants are usually quite low. There are rather many reports on plant concentrations in the scientific literature, though it might often be difficult to discriminate between amounts possibly present as not easily washable surface dust contamination or REEs contained in plaque around roots. Concentrations reported vary several orders of magnitude. Therefore, it is difficult to communicate any ‘typical’ concentrations of REEs in organs of vascular plants (Tyler, 2004).

Uptake and translocation of REEs in plants

In general, a higher availability of REEs causes a higher REEs uptake by plants. The availability of REEs in soils is closely related to the water soluble and exchangeable fractions of REEs, and thus dependent on physico-chemical soil properties such as pH, Eh, CEC, and clay content. A linear accumulation of REEs with increasing plant age found for Norwegian spruce, an important fact perennial crops studies (Wyttenbach et al., 1994).

Ozaki et al. (2002) reported that, about 60 years ago, extremely high concentrations of total REEs (2.300 µg g^{-1}) were found in hickory leaves (*Carya sp.*). Because of the high ability of REEs accumulation, hickory has been regarded as an exceptional plant in the plant kingdom for a long time. Later, however, many more accumulator species were discovered with the increase of researchers’ interest in the elements. For instance, some fern species, such as maidenhair spleenwort (*Asplenium trichomanes*) accumulates 21 µg g^{-1} of Ce and 14 µg g^{-1} of La under natural conditions.

Organic acids are important root exudates in plant adaptation to the environmental stresses. Plants use organic acids to cope with nutrient deficiencies, metal tolerance and plant microbe interactions operating at the root–soil interface. Although many studies have focused on the effects of organic acids on accumulation and phytoavailability of heavy metals, the relevant mechanisms are poorly understood: How do organic acids exert their effects on plant uptake of metals? Are the free metal ions or organic ligand–complexes taken up by plants? What is the coordination environment of intracellular metals in plants? There are no satisfactory answers available at present. With the increasing understanding of the role of organic acids in soil–plant system, understanding their effects on physiological processes become imperative (Han et al., 2005).

Besides roots, uptake of REEs may also occur through plant leaves. Hence, Chua (1998) demonstrated that cerium could be absorbed via the stoma and cuticle, situated on the surface of the leaves of water hyacinth. Afterwards it was distributed to various parts of the plant. Accumulation of cerium in different parts of the plant was in the order of leaves > stems > roots while the leaves accounted for approximately 50% of the concentration of the entire plant. Nevertheless, assimilation of REEs has been reported to vary with each individual element. Thus, a significant correlation between Sc and La could be observed in spruce needles (Wyttenbach et al., 1994), indicating that, with respect to the total soil concentration, the uptake of La is higher than that of Sc. Accordingly, Xu et al. (2003a) found that sole application of La at relatively smaller doses compared to mixtures of REEs results in a substantial accumulation of lanthanum in maize plants. This further supported the assumption that REEs uptake by roots as well as the subsequent transport of the absorbed elements from the roots to the plant tops varies with each REE.

Forms and distribution of REEs in plants

The distribution of REEs among main organs of vascular plants differs considerably. However, roots have usually higher concentrations of REEs than other plant organs and this is only partly due to the fact that it might be difficult to liberate soil growing roots from soil particles. Roots of maize and mungbean grown in solution culture accumulated 20 – 150 times higher La concentrations than their shoots (Diatloff et al., 1995b) and similar root/shoot ratios were measured in *Agrostis capillaries* grown in soil cultures, also after vigorous rinsing of the roots. Many studies have shown decreasing REE concentrations in the order: root > leaf > stem > grain of fruit in a variety of crops such as maize, wheat, rice, and paprika. Also in trees, e.g. citrus, the highest REE concentrations are usually found in roots. REEs in seven tropical tree species were also mainly accumulated in their roots, through Ce tended to be concentrated in the bark (Tyler, 2004).

Foliar application of REEs can take up by plants, and there indications that REEs may be translocated from leaf to root, as studied in maize (Wang et al., 2001b). Rates also seem to differ considerably both between plant species and REE elements. Rates of translocation in paprika (*Capsicum annuum*) were similar for LREEs and HREEs, but in leaves of rape (*Brassica juncea*) they were one to two orders of magnitude higher for LREEs than for HREEs (Cao et al., 2000). In fern *Dicranopteris linearis* the relative abundance of REEs in the above-ground parts was lower than in the roots (Wei et al., 2001). Much of REEs in the roots is certainly located in cortex or in the ferric plaque precipitate of the root surface. However, a study of root tips of rice and pea demonstrated La and Yb to be located in the xylem and Yb also to the endoderm (Tyler, 2004).

Usually, the concentrations of REEs in plant tissues are ranked as follows: root > leaf > stem > flower > fruit (Ma et al., 1996). However, the distribution pattern of REEs in the fern (*Dicranopteris dichotoma*) is varying according to individual REEs. Lanthanum, Ce, Nd, Dy concentrations are in the order of leaf > root > stem, and those of Pr, Sm, Eu, Gd, Ho, Y are in the order of root > leaf > stem (Hong et al., 1999). The distribution of REEs in plants may also be influenced by factors such as application method, type of plant tissue, and the concentration of REEs in substrates. REEs can form chelates compounds, these chelates can combine with the plant components such as proteins, nucleic acids, amino acids, nucleotide acids, etc (Zheng and Chu, 1987). REEs can also combine with pigments and cellulose (cited from Hu et al., 2004).

Accumulation of REEs in plants

About 60 years ago (as mentioned before), extremely high concentrations of total REEs (2.300 µg g^{-1}) were found in hickory leaves (*Carya sp.*) (Robinson et al., 1958). Because of high ability of REEs accumulation, hickory has been regarded as an exceptional plant in the plant kingdom for a long time. Later, however, many more accumulator species were discovered with the increase of researchers' interest in the elements (Koyama et al., 1987). For instance, some fern as maidenhair spleenwort (*Aspenium trichomanes*) accumulate 21µg g^{-1} of Ce and 14 µg g^{-1} of La under natural conditions (Ozaki et al., 2000). Another accumulator species, autumn fern (*Dryopteris erythrosora*), exhibited enhanced growth following addition of La to a culture medium (Ozaki et al., 2002).

Tyler (2004) reported that several pteridophytes (ferns) are known to be particular accumulators of REEs. Strong positive concentration anomalies of La and Ce were reported in at least 9 species of the genera Dryopteris, Asplenium, Adiantum and Dicranopteris in a Japanese study comprising 96 species of ferns (Ozaki et al., 2000). Leaf mesophyll tissue contained 10– 40 µg g^{-1} dry weight of La and 3–30 µg g^{-1} of Ce in the accumulators, compared to 0.003–2.7 and 0.076– 3.6 µg g^{-1}, respectively, in the other species studied. When accumulators and non-accumulators were compared, the latter contained relatively much more Y than other REEs (Ozaki et al., 2002). *Dicranopteris dichotoma* from a rare-earth area in China had total REE concentrations of 0.68–3.36 µg g^{-1}, though with an overrepresentation of the LREEs in the fern biomass compared to soil and also compared to other vascular plants studied (Wang et al., 1997).

Many studies have reported REE accumulation in different types of cereal crops (Lao et al., 1996) or in the different parts of plants (Liu et al., 1997a). Reports also can be found on the time-dependent accumulation of REEs in plants after their agricultural application (Liu et al., 1997b). Unfortunately, these studies have been carried out mostly at a single concentration level and there has been no dose–effect relationship reported up to now. In addition, the reported behavior of REEs in soil–plant systems is often contradictory (Peng and Wang, 1995) and very little information has been given so far on the potential accumulation of REEs in edible parts of plants under the present application practices, where an REEs mixture is being applied through foliar dressing (Wang et al., 2001c).

A higher availability of REEs causes a higher REE uptake by plants. Adding chelating agents could reduce the REE uptake of one accumulator fern, whereas no effect was observed for non-accumulator species (Ozaki et al., 2002). A linear accumulation of REEs with increasing plant age was found for Norwegian spruce (Wytternbach et al., 1994), a fact that is important when studying perennial cops. Relevant for plant uptake in this context is also whether REEs are naturally abundant or exogenously applied. So, 81 – 97% of the applied La was plant available but only 25 – 56% of the naturally abundant element (Stokes et al., 2001).

In addition to essential nutrients, plant absorbs many other elements, which enter the food chain when plants are consumed by humans and animals. However, the ability of plants to accumulate REEs is poorly documented. Diatloff et al. (1995b) found that very high root La and Ce concentrations were found to occur at quite low solution La or Ce concentrations. For example, at 0.8 μM La (0.11 $\mu g\ g^{-1}$) the La concentration in corn roots was 1500 $\mu g\ g^{-1}$, whilst that of mungbean was 2600 $\mu g\ g^{-1}$. Preliminary micro-analysis of thin sections from mungbean roots indicated that the La was found primarily in root cell walls rather than inside the cells. Plants shoots contained very much lower La and Ce concentrations than roots. When nutrient solutions contained from 0.2 to 1.4 μM La (0.03 – 0.2 $mg\ L^{-1}$), concentrations of La in the shoots ranged from 9 to 16 $\mu g\ g^{-1}$ for corn and 34 to 52 $\mu g\ g^{-1}$ for mungbean. These values may be compared with 60 mg kg La found by Wheeler and Power (1995).

Influence of REEs on plant metabolism

Although there is no clear evidence to show that REEs are essential for plants to grow, many studies suggested that REEs could stimulate plants to absorb, transfer and assimilate nutrients (Pang et al., 2002). Ning and Xiao (1989) reported that after using REEs as fertilizers, the absorption of rice for N, P and K was increased by 16.4%, 12% and 8.5%

respectively. The absorption of sulfate by soybeans was also augmented after the application of REEs. Lai et al. (1989) found that tomatoes absorb 8.13% more NO_3^- after blending seeds in 50 mg L^{-1} REEs by the ^{15}N trace technique. Tang and Tong (1988) reported that P and K contents are enhanced 10.3% and 15.4% after spraying tomato seedlings by 5 mg L^{-1} $CeCl_3$. These results suggest that the effects of REEs on improving the absorption of nutrient elements depend upon the methods used in treating the plants. Spraying REEs on plants is commonly thought to be better method than blending seeds in REEs (Wang, 1995).

There are some reports in the literature on the physiological effect on REEs fertilizes, particularly those of membrane stabilization, improvement of hormone effectiveness, growth response to coleoptile segment, better nitrogen fixation efficiency and reduction in water loss by the plants (Wen et al., 2001). However, it is acknowledged that the physiological processes of plants are very complicated. In addition, many factors, such as soil properties, plant species and weather conditions can be also influencing the physiological processes. Therefore, the mechanism of increasing of production and physiological process related to the REEs fertilizer application remains obscure. The impacts of REEs fertilizers application on the environment have been also seriously considered in the literature (Wen et al., 2001).

Wen et al. (2001) reported in a field study about the distribution and bioaccumulation of REEs in wheat, rice, and vegetables grown in four provinces, located in southern and northern China after application of REEs fertilizer at different levels. They found that accumulation of REEs in different parts of plants follow the order: root > leaf > stem > grain (Table 2.13).

Positive, negative, or nil effects of REEs on plant growth and crop yield were observed in culture experiments and field experiments in the former Soviet Union (Savostin, 1937; Kogan, 1973) Romania (Korovitz, 1965; Korovitz, 1974) Bulgaria (Evanova, 1964; Evanova, 1970) the United States (Guo et al., 1988) Japan (Kawasaki, 1980) the United Kingdom (Andrew, 1983) the Philippines (Alejar et al. 1988) Australia (Diatloff et al. 1993; Diatloff et al. 1995a; Diatloff et al. 1995b; Diatloff et al. 1995c; Diatloff et al. 1995d; Diatloff et al. 1996; Diatloff et al. 1999; Meehan et al. 2001) India (Wahid et al., 2000) Malaysia (Aidid, 1994) and China (Guo, 1985; Guo, 1986; Guo, 1987; Guo, 1988; Guo, 1999; Guo et al. 1988; Wang and Zheng 2001; Wang et al. 2003a; Wang et al. 2003b; Wang et al. 2003c; Wang et al. 2003d; Wang et al. 2003e; Wang et al. 2005; Hu et al., 2004).

Similar to other trace elements, REEs exhibit both positive and negative effects on plant growth and development at low and high concentrations, respectively (Shoshi and Takayasu 1987; Hu et al., 2002). The mechanisms of action of the effects of REEs at low concentrations involve significant increases in oxygen evolution, chlorophyll and chlorophyllase synthesis, and photosystem (PS) I and PS II activity. In contrast, it was found that high concentrations of REEs exhibit inhibitory effects on crops, microbes, and enzymes (Chang 1991; Chu et al., 2000a, 2001c; Wang et al., 2005).

Table 2.13: REE content (ng g^{-1}) in edible parts of vegetables, wheat and rice grown in Beijing site (China) with and without REEs fertilizer application (adapted from Wen et al. 2001)

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Vegetables[a]															
Cucumber															
Control	19.1	21	41	21	5	1	11	2	0.8	2	0.4	0.1	0.3	0.1	0.1
Treated	23.4	25	45	23	5	2	13	3	0.8	2	0.6	1.2	0.3	0.7	0.7
Tomato															
Control	4.5	20	15	3	5	0	2	1	0.3	1	0.1	0.3	0.1	0.1	0.1
Treated	6.1	32	43	4	23	2	5	2	0.7	3	0.4	1.5	0.2	0.8	0.2
Cabbage															
Control	71.1	65	99	63	92	12	25	10	8.8	7	0.1	0.9	0.4	0.7	2.2
Treated	101.7	830	682	161	229	31	188	34	17.3	30	2.2	15.8	1.6	9.9	-
Chinese cabbage															
Control	101.7	80	715	250	104	42	68	39	10.6	36	3.5	15.3	0.7	5.6	4.6
Treated	314.2	3524	3831	460	771	105	169	146	51.3	138	13.3	43.3	2.6	16.2	8.6
Wheat[b]															
Root															
Control	525	725	1370	185	567	119	33	119	17	108	23.6	49	12.6	51.7	8.8
Treated	1328	2189	3843	396	1295	297	169	488	153	469	41.4	172	21.8	88.1	45.1
Stem															
Control	52	67	119	12	46	8	7	13	2	10	1.7	7	1.1	7.6	1.5
Treated	69	208	363	36	118	12	6	15	2	11	2.2	3	1.2	7.4	1.3
Leaf															
Control	328	388	695	80	301	58	12	53	7	37	6.7	16	2.9	19.2	2.0
Treated	404	938	1960	297	792	117	29	216	19	10	12.1	50	5.2	35.0	2.0
Grain															
Control	51	74	129	14	44	11	4	12	2	10	2.6	7	0.4	5.4	0.9
Treated	47	63	110	14	44	9	5	10	1	6	1.3	6	0.3	5.0	1.0
Rice[c]															
Root															
Control	1061	628	913	66	133	116	298	187	60	93	33	57	11.7	28.8	31
Treated	860	1621	3218	337	1277	252	154	240	83	187	35	106	14.3	92.1	44
Stem															
Control	9	12	31	3	10	116	298	187	60	93	33	57	11.7	28.8	31
Treated	14	27	39	4	18	297	1169	488	153	469	41	172	21.8	88.1	45
Leaf															
Control	13	42	51	6	15	3	25	11	3	8	1.2	4	0.7	1.4	2
Treated	35	85	94	16	43	6	64	16	5	10	1.1	5	0.9	3.1	4
Grain															
Control	19	46	49	7	15	5	30	9	3	5	0.5	3	0.8	0.8	1
Treated	22	48	47	6	17	5	42	11	3	6	0.2	2	0.7	1.0	1

[a] treated, means applied fertilizer at level of 165 g La ha^{-1}, 305 g Ce ha^{-1} for vegetables.
[b] The applied fertilizer level was 165 g La ha^{-1}, 305 g Ce ha^{-1} for wheat.
[c] The applied fertilizer level was 113 g La ha^{-1}, 209 g Ce ha^{-1} for rice.
Six measurements for each sample, the RSD less than 10%.

Influence of REEs on the stability and function of cytoplasmatic membranes

La^{3+} decreased the production of OH^- by reducing the content of O_2 and H_2O_2, which efficiently alleviated peroxidation of membrane lipids under osmotic stress and protected the membrane from injury of free radicals (Zeng et al., 1999). Thus, La^{3+} increased the tolerance of plant to osmotic stress. La^{3+} inhibited electron transfer from NADH to oxygen in plant plasma membranes, depressed the production of active oxygen radicals, and reduced the formation of lipids peroxides through plasma membrane lipid peroxidation (Zheng et al., 2000). La^{3+} also enhanced the H^+ extrusion by both standard redox system and H^+-ATPase in plasma membranes at certain concentrations (Hu et al., 2004).

Similarly to Ca, REEs have also been shown to affect the stability and functionality of membranes (Mikkelson, 1976; Dong et al., 1993; Qiao et al., 1993). In the review of Brown et al. (1990), which summarized the effects of REEs on membrane stabilization, it was reported that La and other REEs might restrict leakiness by altering membrane characteristics, particularly membrane fluidity (Redling, 2006). Other studies also reported reduced penetration of electrolytes as well as increased membrane stability and integrity due to REEs application to plants (Tian, 1990; Shen and Yan, 2002). It was assumed that this might additionally explain enhanced cold resistance observed in treated plants. Furthermore, by decreasing the penetrability of cell membranes, La was shown to influence the proton release of cells (Qiao et al., 1993). Dong et al. (1993) suggested that REEs might reduce penetration through cell membranes by forming stable complexes with big molecules such as phosphoglyceric acid. Similarly, Ni (1995) who observed that lanthanum chloride might decrease the permeability of plasma membranes also attributed these stabilizing effects on the cell membrane to the interaction of REEs with phospholipids or protein amino acid groups. It was further reported that REEs might replace and compete with Ca for binding sites on proteins and thus affect the stability of cell membranes (Hu and Ye, 1996). However at high concentrations, REEs destroyed the cell membrane stability by increasing cell permeability (Chang, 1991). Another study demonstrated that La and Ce enhanced the concentration of polar and no polar fat in cell membranes which is thought to prevent leaves from aging (Xing and Weng, 1991). In a similar manner, La increased the content of unsaturated fatty acids in wheat settings (Li et al., 1992b; Redling, 2006).

In addition, effects of REEs on reactive oxygen species (ROS) also lead to increased membrane stabilization as it is known that free radicals can destroy the structure of cell membranes. According to Wang et al. (2003b), REEs may inhibit ROS – related lipid peroxidation and oxidation of membrane proteins by binding to hydroperoxides.

Hormonal interactions of REEs

Brown et al. (1990) pointed out that La and other closely related REEs influenced many physiological processes of plants, including hormonal interactions. These influences are particularly related to the synergistic action of REEs with hormones. Low concentrations of Eu (0.001 –1.0 mg. L^{-1}) were found to possess similar functions as plant hormones. As it is reported that REEs may affect hormonal binding by their direct or indirect interactions with their receptors (Enyeart et al., 2002), interactions with hormones have been proposed as one of the most important means by which REEs may influence plant physiological processes such as plant growth (Brown et al., 1990). Additionally, it was reported that REEs might function as potent hormone effectors due to membrane actions (Redling, 2006).

The application of a solution of 1.08 mg L^{-1} $NdCl_3$ significantly promoted induction of GA_3 to α-amylase, and decreased a lag of GA_3 (giberillic acid) induction action (An and Chen, 1994). REEs accelerated also the formation of α-amylase induced by GA_3 in the aleurone layer of wheat seed and increased nutrient transformation. REEs were also identified as regulators of endogenesis hormone (Liu and Liu, 1985). It was suggested that alteration in the attachment of the hormone to binding sites in the cell account for this effect (Taiz and Zeiger, 1998). In addition, after the treatment with 7.5 mg L^{-1} of $La(NO_3)_3$, increased contents of indole acetic acid (IAA) were determined in wheat seedlings (Sheng and Zhang, 1994). It is known that indole-3-acteic acid (IAA), which constitutes the main auxin found in plants, controls many important physiological processes such as cell enlargement and division, tissue differentiation as well as light responses. Another study demonstrated contents of tryptophan, which may be used for synthesis of IAA (Leveau and Lindow, 2005), to be increased in the coleoptiles of corn due to REE application. Furthermore, REEs decreased the enzyme activity for IAA decomposition thereby promoting IAA synthesis, while lanthanum chloride was reported to enhance IAA uptake and translocation (Allan and Rubery, 1991; Redling, 2006).

Influence of REEs on photosynthesis

In agriculture, REEs have been used since the early last century with positive effects on crop productivity, although only a small number of reviews on plant photosynthesis have become available internationally. The literature on the effects of REEs on plant photosynthesis is predominantly written in Chinese. The application of mixed REEs nitrates turned out to be beneficial for photosynthesis. The supply of REEs to plants increased photosynthesis intensity and net photosynthetic rate by 11-31% (Xiong et al., 2000). The translocation of photosynthetic products can also be influenced by REEs. Xiong (1986) reported that the application of REEs increased the translocation of photosynthetic production by 17-149%. Besides photosynthetic rate, REEs could also influence the translocation of photosynthetic products. Increased translocation from the leaves to the roots of 5.6-8.2% was reported by Bai and Deng (1995). The effects of REEs on plant photosynthesis are related to chloroplast development, chlorophyll content and enzyme activity (activities of PS I, PS II and RuBPcase, Liu et al., 2004a). In experimental studies REE treated wheat plants increased the number of chloroplasts, and the density of canaliculus (Gao and Xia, 1988).

Increases in both the chlorophyll content and the photosynthetic rate by 4.7% and 31.8%, respectively were observed after the seeds of sugar beets were mixed with REEs (Xie and Chen, 1984). Several further studies also demonstrated increases in net photosynthetic rate of 11 - 31% and increased photosynthesis intensity after the supplementation with REEs to plants (Chief Office of Helongjiang Farm, 1985; Chen, 1991; Cui and Zhao, 1994); (Xiong et al., 2000). However, the photosynthetic rate cannot only be increased by mixtures of rare earths but also by single REEs. Accordingly, sole application of cerium also increased chlorophyll contents and photosynthetic rate in spinach (Fashui et al., 2002). At concentrations of more than 15 µg g^{-1} La, a decrease in chlorophyll contents as well as in chlorophyll a and b was observed in rape (Zeng et al., 2001). In tea plants, was also shown that REE fertilizers could enhance photosynthesis (Wang et al., 2003e). According to that, a former study demonstrated that rare earths might increase the translocation of photosynthetic products by 17-149% (Xiong, 1986; Redling, 2006).

Hong et al. (2002) also showed that La^{3+}, Ce^{3+} promoted growth, increase chlorophyll content and photosynthetic rate of spinach. La^{3+}, Ce^{3+} might substitute Mg^{2+} for chlorophyll formation of spinach under Mg^{2+} starvation. La^{3+}, Ce^{3+} significantly improved PS II formation and enhanced electron transport rate of PS II. Spectroscopy proved that La^{3+}, Ce^{3+} involved in the distribution of porphytin rings. Liu et al. (2004a) proved that Nd^{3+} enhanced electron transport rate of PS II of spinach. It may be the results from the combination between Nd^{3+} and the chlorophyll ($P68^{+}$) or pigment-protein and polypeptide complex which promoted charge recombination of $P680^{+}$ and the reduced pheophytin (Hong et al., 2002). The relationship between Nd^{3+} and photosynthesis still needs further research.

Effect of REEs on stress-related plant enzyme activities

Changes in both activity and content of several plant enzymes have been observed in plants treated with REEs and therefore considered as possible explanations for the effects of REEs on plants. Decreased activity of the sucrose transform enzyme of 34 – 84% after sugar beet plants were sprayed with 0.1 to 500 µg L^{-1} of REEs was found and, it was suggested that changes in enzyme activity account for increased sugar contents (Tian, 1988; Bai and Chen, 1989; Xiong et al., 2000). Significant increases in the content of glucose were reported in sugar beet leaves after foliar application of REEs. Stimulation of enzyme activity due to REE supply was also highly assumed by Zhimang et al. (2001) after noticing a good correlation between accumulation of REE and activity of glutamic oxaloacetic transaminase (GOT) with correlation coefficients = 0.922 (Redling, 2006).

In plants, the GOT activates the reaction α-ketoglutarate + L-aspartic acid → L-glutamate acid + oxaloacetic acid, which involves both the nitrogen and the amino acid metabolism and may change organ functions (Xu et al., 1998). Additionally, since oxaloacetic acid contains carboxyl and hydroxyl groups (Fell et al., 1997), binding to them may facilitate REEs uptake to the plant tops. Along with enhanced respiratory rate, Hong et al. (2000) reported increased activities of superoxide dismutase, catalase, and peroxidase as well as decreased superoxide O_2^- in rice seeds treated with La nitrate. Thus, it was suggested that this might reduce the permeability of plasma membranes. Other studies demonstrated increased nitrate deoxidase in soybean leaves when REEs were applied as seed dressing at the early period of seed setting or during flowering (Chief Office of Helongjiang Farm, 1985; Chen, 1991; Xiong et al., 2000; Redling, 2006).

After being sprayed with 0.1 to 500 µg L^{-1} of REEs, the sucrose-transform-enzyme decreased by 34 – 85% in sugar beet leaves. Also in sugar beets sprayed with REEs, the content of deoxidized-sugar varied from 5.8 to 25 mg with a control level of 38 mg and the contents of glucose and fructose were significantly increased (Xiong et al., 2000). Seed dressing with a REE solution increased nitrate deoxidase in soybean leaves from 16.7 NO_2^- µg. g^{-1} (FW) to 25.3 NO_2^- µg. g^{-1} (FW). Also in soybean leaves the application of REEs during flowering increased nitrate deoxidase from 5.84 NO_2^- µg.g^{-1} (FW) to 6.17 NO_2^- µg.g^{-1} (FW), and from 0.93 NO_2^- µg.g^{-1} (FW) to 1.53 NO_2^- µg.g^{-1} (FW) later during the early period of seed setting (Xiong et al., 2000; Chen, 1991; Chief Office of Helongjiang Farm, 1985). In cotton leaves the application of REEs increased nitrate reductase by 19% and the content of NO_3-N by 26% (Zhao, 1988; Hu et al., 2004).

Liu et al. (2004b) studied the effect and the mechanism of action of La, Ce and Nd on the activities of superoxide dismutase (SOD), catalase (CAT) and peroxidase (POD) of aged spinach seeds using $LaCl_3$ (0, 8.8, 17.5, 35, 70 and 140 µg L^{-1}) $CeCl_3$ (0, 0.2, 0.4, 0.7, 1.4, 2.8 and 5.6 µg L^{-1}) and $NdCl_3$ (0, 9, 18, 36, 72 and 144 µg L^{-1}) treatments (Liu et al., 2004b). The SOD, CAT and POD activities of germinating aged spinach seeds treated with La^{3+}, Ce^{3+}, and Nd^{3+} are higher than that of the control. The most effective treatment concentration of La^{3+}, Nd^{3+} (70 and 72 µg L^{-1}, respectively) increases SOD activity 3.7, 4.3 times compared to the control. The results indicated that La^{3+}, Ce^{3+} and Nd^{3+} treatments increased the SOD activities of germinating aged spinach seeds. About CAT activity, the highest activities are still made by the treatment of 70 µg L^{-1} La^{3+}, 72 µg L^{-1} Nd^{3+} and 2.8 µg L^{-1} Ce^{3+}, which are 7.4, 8.8 and 9.7 times of the control (Liu et al., 2004b). It proved that La^{3+}, Ce^{3+} and Nd^{3+} increased the CAT activity of germinating aged spinach seeds, and Ce^{3+} treatment is most effective. The most effective treatment concentration of Ce^{3+} (2.8 µg L^{-1}), Nd^{3+} and La^{3+} (72 and 70 µg L^{-1}) increased POD activities 3.5, 2.5 and 2.0 times compared to the control.

Effect of REEs on water use efficiency

Wen et al. (1992) investigated the effects of REEs on drought tolerance and yield by mixing 1 kg of corn seeds with 1-5 g of REEs in form nitrate. The lowest water potential measured in corn leaves was observed when 1 kg seeds were mixed with 3 g REEs in form nitrate. This was accompanied by a significant increase in corn yield of 17%. Proline has a strong ability for hydration. Thus the increase of the proline content in plants helps to hold water during drought periods. The proline in sugarcane was reported to increase after REEs application (Yu and Liu, 1992). At the same time the free-water (FW) content in leaves decreased and tied-water (TW) increased, decreasing the ratio RW/TW improving the drought tolerance of sugarcane (cited from Hu et al., 2004).

Meehan et al. (2001) investigated the effects of La application and water supply on barley. Under the condition of 50% of field capacity the dry matter of barley was 18% greater in plants treated with 5 kg ha^{-1} and 10 kg ha^{-1} of La than in the control plants. No differences were observed at 100 and 75% of field capacity. Another experiment demonstrated also that La application to well-watered plants did not exhibit significant differences in water use efficiency, but under water deficit conditions the water use efficiency was 21% higher than the control. Also under drought conditions, an increase of 33% in the total number of tillers was observed (Hu et al., 2004). In experiments conducted by Reddy et al. (2001), the physiological responses of barley and wheat to treatments with REEs were different. In barley, water and osmotic potential increased and turgor was maintained. In wheat both water and osmotic potential decreased but turgor was maintained (Hu et al., 2004). The relative water content was affected in both barley and wheat indicating that cell hydration was not perturbed.

Influence of REEs on dry matter production

The results from the few existing studies on the effect of REEs on plant growth are conflicting. Early reports indicated that REEs were inhibitory to plant growth. For example,

La^{3+} and Nd^{3+} were found to inhibit the elongation of oat coleoptiles sections. Colloidal lanthanum caused an almost complete inhibition of cell division and root elongation in the root tips of barley plant (Hu et al., 2004). More recently, Diatloff et al. (1995a) also reported that root length of corn and mung bean decreased with increasing concentration of La and Ce. In a solution culture with wheat, the estimated toxicity threshold of La^{3+} was 0.09 mg g^{-1} of dry matter of tops, 3.0 mg g^{-1} of dry matter for roots. Plant toxicity, which reduced yield by 50%, of La^{3+} was in the order Mn < Zn < Fe < La < Cu (Wheeler and Power, 1995).

Essential nutrients and beneficial elements are often toxic to plants when supplied in excess. The identification of threshold concentrations for the toxicity of La and Ce to plants provides an indication of the concentration below which beneficial effects may occur. Change in root length provides a rapid and sensitive indicator of toxicity. Toxicity of plants to aluminium (Al), a trivalent ion similar to La and Ce can be alleviated through complexation by humic acid (HA) and fulvic acid (FA) that are present in soil solution (Harper et al., 1995). There is evidence that REEs also form strong complexes with HA and FA (Bidoglio et al., 1991), but it is not known whether such complexes can overcome phytotoxic effects of La. Consequently, the effects of varying La or Al concentrations (0 to 30 µM) on corn root elongation were examined in the presence and absence of HA and FA (Diatloff et al., 1995b).

Common yield responses of plants to rare earth application are to be in the order of 5 to 15% and sometimes even higher (Xiong, 1995). In addition to plant yield increases, improvements in product quality, comprising increased sugar content in sugar cane, increased vitamin C content in grapes and apples and increased fat and protein content in soybean (Brown et al., 1990; Wan et al., 1998) have also been reported for a wide range of crops. Furthermore, rare earth supplementation was reported to decrease the content of chemical residues in several crops such as rice, orange, watermelon, grape and pepper (Redling, 2006). Although nowadays mostly mixtures of REEs are used in Chinese REE fertilizers, in experimental designs both single and mixed REEs were applied in order to evaluate their potential. Growth promotion after REE application was also observed in potatoes in pot experiments (Jie, 1987). Both seed dressing and foliar application increased yield of potatoes by 6% and 5%, respectively (Jie, 1987). Results obtained from 43 field trials using 2880 kg ha^{-1} showed an increase in tuber yield of potato by 13.8%. Spraying of 750 g REEs per ha increased starch yield by 1.5% and the ascorbic acid ($C_6H_8O_6$) concentration in the tubers by 38.9 µg g^{-1}. Thus, REEs have been shown to promote potato growth, improve tuber formation and growth as well as starch accumulation (Chen and Zheng, 1990).

Several solution culture experiments with sugar beet seedlings have been performed by Feng (1987). The results showed that in 48% and in 32% of all cases, root length and plant height respectively could be increased by the application of REEs at concentrations of 0.01% up to 0.1%, whereas in 10-55% of all cases dry weight was also increased. Furthermore, advanced germination and rhizogenesis were found in sugar beet seedlings after a two-year storage period. At high concentrations, however, inverse effects were noticed. Further studies showed that sugar beet seeds without lignified septals presented higher germination rates compared to those with lignified sepals. It was therefore suggested that the lignified sepal might disturb the uptake or translocation of rare earths in plants (Redling, 2006).

It was concluded, that the impact of REEs on plant development depends on the growth medium. La in concentrations from 0.49 to 10.02 mg L^{-1} increased dry-matter production of barley, canola, and ryegrass by up to 90%, 38%, and 78%, respectively, when the plants were cultivated under greenhouse conditions in perlite with Hoagland's nutrient solution (Peverill et al., 1997). When plants were grown in soil, yields were unaffected, except in a loamy sand, where the yield was increased under drought conditions. Also, in the field, virtually no effect of La on biomass production was observed (von Tucher and Schmidhalter, 2005).

However, influence of REEs on nutrient metabolism in plants including beneficial effects of REEs on absorption, transfer and assimilation of nutrients in plants have been reported, whereas Chang et al. (1998) demonstrated promoting as well as inhibiting effects of REEs on velocity and physics of nutrients uptake by crops (Redling, 2006).

It is not surprising that REEs strongly affect ionic interactions with the plant cell (Hu et al., 2004). REEs clearly influence the ionic fluxes into plant cell in different ways. These fluxes in turn may be expected to affect several plant processes (Hu et al., 2004). It could be distinguished that the following experiments have conflicting data. These controversial results may be attributed to different analytical methods employed, but may be also indicate the complexity of actions involved in the effects of rare earths on plant physiological processes such as nutrient uptake. Nevertheless, despite different results, it is quite obvious that REEs have the ability to affect ionic fluxes into cells, thus their concentrations in different ways and to various extents. Changes in ionic fluxes as well as in the mineral composition may in turn affect several plant physiological processes. Yet it needs to be kept in mind that results from several Chinese studies are lacking detailed information (Redling, 2006).

It has been assumed that the effect of REEs on nutrient elements depends on the method of application. In cotton, uptake of N was shown to be accelerated by La application in solution culture experiments (Zhu, 1986). Furthermore, both soil culture experiments (Zhu and Hu, 1988) and field trials (Jie and Yu, 1985; Zhu, 1992) demonstrated that REEs enhanced N uptake by wheat plants after treating them with a mixture of REE-nitrate, and Jie and Yu (1985) reported improved N utilization to be in the range of 20 - 26%. REEs applied to Chinese date trees increased the absorption of N and Zn (Chang, 2006). The application of REE containing fertilizer to rice increased absorption of N by 16% (Ning and Xiao, 1989). Additionally, sulfate absorption by soybeans was also found to be enhanced. While, seed dressing with REE-nitrate has been shown to increase the contents of NO_3^- in corn by 37% (Cui and Zhao, 1994), decreased N contents were observed after application of La alone (Diatloff et al., 1995a). A like, noncompetitive inhibition of NO_3^- uptake as well as reduced assimilation of NH_4^+ was observed in rice after the addition of La and Ce (Hu and Zhu, 1994). In contrast to that, increased absorption of nitrates was also reported in sugarcane (Kuang, 2006). The leaf nitrogen balance was decreased after the application of REE-nitrate fertilizer. Additionally, an increase in total leaf nitrogen, a fractionation from nitrate nitrogen to amino nitrogen and the free amino acid pool was observed. An accelerated transfer of N from inorganic to organic forms was also described by Pang et al. (2002). This is considered to be beneficial for both the protein synthesis as well as the regulation of nutrient balance (Redling, 2006).

Thus besides nutrient uptake, REEs might also influence the metabolism of nutrients in plants. Enhanced nitrate reductase (nitratase) activity was noted in peanuts and tomatoes due to spraying of REEs (Guo et al., 1988). Furthermore, after mixing seeds with REEs nitrate reductase enhancements of 37 - 75% were observed in leaves of winter wheat, while at the same time yield increased by 16% (Yang and Zhang, 1986). After application of REEs, the number of root nodules increased significantly and the activity of nitrogen fixation were improved by 24%. Consequently the absorption of N by legumes was enhanced significantly (Wu et al., 1984).

In addition to minerals, the content of amino acids could also be affected by REEs. The application of 870 mg L^{-1} La chloride increased glutamine and alanine contents by 66% and 68% respectively in cucumber (*Cucumis sativus*) (Chang, 2006). Significant increases in amino acid contents especially aspartic acid, serine and arginine were also observed in leaves of date, Chinese date, after REEs were applied (Sun et al., 1998). In accordance with the dose-dependent effects of rare earths on plant growth, different concentrations may also influence their effects on nutrients uptake. Besides dose-dependency, these effects have also been shown to differ among the individual REEs. While La was able to increase N, P and K uptake in plants at low concentration, Ce only increased N uptake leaving P and K uptake unaffected.

Pr increased the absorption of N and P but decreased potassium uptake. While promoting the absorption of N, Nd greatly inhibited phosphate and potassium absorption (Chang, 2006).

Influence of REEs on yield and quality of crops

REEs have been used in agriculture since the early 20th century, but only recently few reviews of REEs effects on crop performance have become available internationally. REEs effects on growth, yield, and quality of some selected crops have been reviewed (Table 2.14).

Table 2.14: Yield increases (positive increasing effects and relative to control) observed after REE applications to different crops (adapted from Hu et al., 2004)

Crop	Country	Yield increase (%)	References
Sugar beet	Bulgaria	17 - 24	Evanova (1964)
Sugar beet	China	7	Guo et al. (1998)
Wheat	China	6 - 17	Jie and Yu (1985), Yang (1989a), Yang (1989b)
Rape	China	4 - 48	Ren and Xiao (1987), Cai and Zheng (1990)
Potato	China	5 - 6	Jie (1987), Chen and Zheng (1990)
Soybean	China	8 - 9	Qiao and Zhang (1989), Xiong et al. (2000)
Cotton	China	5 - 12	Guo, et al. (1988)
Rice	China	7	Wang (1995)
Corn	China	9 - 103	Xiong et al. (2000)
Peanut	China	8 - 12	Guo (1985)
Tobacco	China	8 - 10	Guo (1985)
Rubber	China	8 - 10	Guo (1985)
Sugarcane	China	10 - 15	Guo (1985)
Cabbage	China	10 - 20	Guo (1985)
Litchi	China	14 - 17	Guo (1985)
Grape	China	8 - 12	Guo (1985)
Barley	Australia	18 - 19	Reddy et al. (2001)

Xiong (1995) also reported about the species of plant, which treated with REEs and the effects of treatment and listed in Table 2.15.

Table 2.15: Effects of REEs on crops pasture grasses, and trees (adapted from Xiong, 1995)

Name	Increase in yield		Effect on quality of produce
	Extent (%)	REE application (Kg ha^{-1})	
(1) Cereal Crops:	7-14	100	
Maize	6-12	465	Weight per 100 grain increased by 0.2-0.35 g
Wheat	6-15	420	Lysine in grain tended to increase
Rice	5-15	300	
Industrial Crops:			
Rubber Tree	6-20	150	Dry rubber reached the first grade
Tobacco	7-16	320	Grade rate elevated by 10%
Soybean	6-12	150	Protein and oil tended to increase
Peanut	8-15	320	
Cotton	5-12	90	Weight of single boll increased by 0.1 g, 2.5% span length of fiber increased by 0.1-0.4%
Ramine	7-15	80	Fiber count increased by 10-15%
Flax	Stem 8-12 Seed 10-14	150	Fiber increased by 10-15%
Rape	14-24	80	Oil content increased by 2%
Fruits:			
Apple tree	10-22	500	Sugar content 0.5-10%, vitamin C increased by 20%, cyanine doubled
Chinese Gooseberry	10-25	6 (single plants)	Sugar content increased by 1.3-2.9%, vitamin C increased by 40-42% mg 100 g^{-1}
Banana	8-14	1350	Sugar content increased by 3-4%, vitamin C increased by 4.6%
Vegetables:			
Potatoes	10-14	1500	Starch content increased by 1%
Chinese Cabbage	10-20	7500	Head-forming rate elevated, 3.5 leaves/head
Cucumber	13-15	750	Reducing sugar increased
Edible Fungus	10-13	1-1.5 kg m^{2-}	Amino acids increased by 40%
(2) Pasture Grasses			
Siberian Wild Rye	Hay 15-25 Seed 10-15	750	Crude protein increased by 3-9%
Alfalfa	Hay 5.2-33 Seed 10-15	750	Crude protein increased by 3-10%
Shadawang	Fresh grass 10-20		

(3) Forestry

Name	Results	Effect on quality of produce
Changbai Larch	Stocking percent increased by 6-12%, sapling yield increased by 6000 plants per mu (1mu=1/15ha)	Grade of stock raised, adverse resistance enhanced
Scotch Pine of Mongolian Variety	Stocking percent increased by 6-10%, sapling yield increased by 2000 plants per mu	Ditto
Red Pine	Sapling yield increased by 12.8%	Ditto
Small Black Poplar	Stocking percent increased by 10%, sapling yield increased by 2500 plants per mu	Ditto
Chinese Pine	Sapling yield increased by 10%	Ditto
Mulberry	Stocking percent increased by 15%, leaf yield increased	Soluble sugar increased by 35%

2.3 Ecotoxicology of REEs

Most of the studies on the response of crops to REE application were focused on their beneficial effects, and the phytotoxicity of REEs is still poorly documented (Guo, 1987; Xiong, 1995; Brown et al., 1990). However, some of the studies reported REE accumulation in crops and soils after different concentrations of REE application (Wang et al., 2001; Zhang and Shan, 2001; Xu et al., 2002). The research of Diatloff and Smith (1995) also showed that REEs were toxic to plants. A 50% reduction in corn root elongation was evident with 4.8–7.1 mmol L^{-1} La (0.7 – 0.9 µg g^{-1}) or 12.2 mmol L^{-1} Ce (1.7 µg g^{-1}) in solution culture. Work of Xie et al. (2002) also indicated that rice straw weight and total grain weight were significantly decreased with high La concentration (≥ 1.5 mg L^{-1}) in solution. These results implied the environmental risk of excessive REE application, but their work was conducted under solution culture condition and could not actually show the growth of plants in different soils contaminated by La (Zeng et al., 2006).

Due to their similar effects to heavy metals and potential risk of application, control of REE contamination should be taken into account. The critical concentration of La with regard to environmental safety was suggested to be 42 µg g^{-1} in red soil and 83 µg g^{-1} in paddy soil according to 10% yield decrease in the rice pot experiments (Zeng et al., 2006). The damage to rice caused by La was more serious than those by Cr(III), Cu, Zn, and Pb but less serious than those by Cd and Cr(VI) (Zeng et al., 2006).

Accumulation of proline, increase of POD activity and cell membrane permeability, and decrease of chlorophyll and chlorophyll a/b ratio were also observed in rice subjected to excessive heavy metals (Chen and Kao, 1995; Qin et al., 1994; Shi, 2004). Moreover, compared with the rice responses to heavy metals, those to La were quite similar; that is, there was a slight increase at lower added concentrations but a great decrease at excessive added concentrations. Chlorophyll a/b ratio and leaf peroxidase (POD) activity might therefore provide useful criteria for early diagnoses of phytotoxicity of soil contaminated by La (Zeng et al., 2006).

The term ecotoxicology was coined by Truhaut in 1969, as a natural extension from toxicology, the science of effects of xenobiotics on individual organisms, to the ecological effects of pollutants. The term was derived from the words ‘ecology’ and ‘toxicology’. While toxicology is concerned with effects on single organisms; ecotoxicology is concerned with effects on a whole ecosystem (Moriarty, 1988). Most sources of environmental pollution are of anthropogenic origin with a great majority of pollutants originating from industrial discharges. Thus metals and metal species constitute a significant part in environmental contamination (Yousos et al., 2001).

Since, up to now, Chinese farmers have used REEs-containing fertilizers as base fertilizers (with N-fertilizers) to improve crop production, currently only studies are available on the combined effects of nitrogen and lanthanides (Xu and Wang, 2001). In addition, only little attention has been paid to the accumulation of REEs in crops after years of application. For the safety assessment of agricultural application of REEs, it is important to study the dose-dependent accumulation of individual REEs in crops upon addition of such fertilizers, and the corresponding mechanisms by which the REEs can enter the plants (Xu et al., 2003).

Many studies have reported that REEs accumulate in different types of cereal crops (Liu et al., 1997a; Lao et al., 1996) or in the different parts of plants (Liu et al., 1997a; Lao et al., 1996). Reports can be found on the time–dependent accumulation of REEs in plants after their agricultural application (Zhang et al., 1993; Liu et al., 1997c). Unfortunately, these studies have been carried out mostly at a single concentration level and no dose-effect relationship has been reported up to now. In addition, the reported behavior of REEs in soil-plant systems is often contradictory (Peng and Wang, 1995) and very little information has been given so far on the potential accumulation of REEs in edible parts of plants under the present application practices, where REEs mixture is being applied through foliage dressing (Wang et al., 2001a).

Since the early 1980s, the amount of REEs used in Chinese agriculture has increased, reaching a few thousand tons each year. In recent years, REE complex fertilizers, whose main REE components were La and Ce, have been extensively applied and directly used on soils (Zhang et al., 1995). Therefore, the amount of REEs put into the environment increased rapidly during these years. However, results of hygienics research showed that exposure to excess REEs could cause significantly negative effects on the function of the immune, circulatory, digestive, and nervous systems of humans especially on the score of IQ, physical growth, and development of children, and could even cause cancer (Yuan et al., 2003; Fan et al., 2002, 2003). So the ecological risk of REEs in the field has to be assessed and managed by drawing limits accordingly (Zeng et al., 2006).

Toxicology of REE fertilizers

There are basically three kinds of Chinese fertilizers, each of which contains different REEs. They are: Changel-Yizhisu (CY), which contains nitrate forms of REEs (Table 2.16); Nongle (NL) (Table 2.17), which contains chloride forms of REEs and its main component belongs to REEs (38% as oxide, RE_2O_3); and MAR (rare earth complex of mixed amino-acids), which contains 17 amino-acids together with elements of La, Ce, Pr and Nd (Pang et al., 2002).

Table 2.16: Single REEs content (%) in Changel-Yizhisu, CY (adapted from He et al., 1998)

La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Total RE_2O_3
19.8	4.66	1.86	5.40	0.34	0.07	0.08	32.2

Table 2.17: Single REEs content (%) in Nongle "NL", $RECl_3$ x xH_2O (adapted from Redling, 2006)

La_2O_3	Ce_2O_3	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Insoluble	Total RE_2O_3
32.0	61.0	6.5	0.50	0.34	0.07	0.08	< 0.3	45.1

Since the 1970s, scientists in China have applied inorganic compounds of rare earths (REEs), such as $RE(NO_3)_3$, to agricultural soils in the form of microelement fertilizer and studied their effects on crop yield and quality and the accumulation of REEs in the soil. According to analyses of the concentrations of individual REEs in field-grown maize after the application of REE-containing fertilizer, the dosage of REEs (< 0.23 kg ha^{-1} $year^{-1}$) currently applied in China hardly affects the safety of maize growing in arable soil, even over a long period (Xu et al., 2002; Wang et al., 2003d).

More and more REEs are widely applied in agriculture as microelement fertilizers in China because of their abilities to improve quantities and qualities of crops (Liao et al., 1994; Wyttenbach et al., 1998). REE concentrations remarkably increased in soil ecosystems and have become a serious environmental problem (Gu et al., 2001). In the last 20 years, many researchers have reported about distribution, transformation and translocation of REEs in soil and plant systems (Sun et al., 1999; Yang et al., 1999). Recently, more and more attention has been given to the possible adverse effects of long-term REEs application. For example, concerns exist on the harmful effects of REEs on the integrity of soil ecosystems and on their potential toxicity for aquatic systems (Wang et al., 2001a).

A widespread application of REEs may lead to scattering and bioaccumulation in the environment, particularly in agricultural production, which leads to transfer through the food chain to the human body. Velasco et al. (1979) suggested that, at high dosages, REEs might become harmful in the environment. It has been predicted that an industrial and agricultural utilization of REEs and the resulting environmental contamination would rapidly grow in the next few decades (Volokh et al., 1990; Xu et al., 2002).

Application methods of REE fertilizers

One of the important applications of REEs is in agriculture. Millions of tons of fertilizers containing REEs are used worldwide for increasing agricultural productivity (Bremmer, 1994). In China, the fertilizer containing REEs for agricultural use was estimated to cover (16 to 20) $\times 10^6$ hectares in 1995 and the yearly consumption was estimated to cover more than 3×10^6 hectares since 1998 (Guo, 1999). Widespread use of fertilizers containing REEs in agriculture results in increase of REEs concentrations in plants and soils. Despite the reported increase in agricultural yields by application of these fertilizers, the possible long-term hazardous environmental effects are worth comprehensively investigating. The long-term and continued introduction of certain metals would interrupt the balance in the environment, hence causing serious environmental problems (Wang et al., 2003c).

REEs have been used as fertilizers by blending seeds, immersing seeds and spraying on leaves. Table 2.18 shows examples to the application methods and the amount of REEs that were used (Pang et al., 2002). Spraying REEs on plants is commonly thought to be a better method than blending seeds in REEs (Wang, 1994).

Table 2.18: Application methods and the used concentrations of REEs for some selected crops (adapted from Pang et al., 2002)

Crops	Application methods and used amounts of REEs	Total amount ($g\ ha^{-1}$)*
Wheat	Spray: 600 mg L^{-1} (end of March until 10 April)	240
Maize	Blending seeds: 3 g kg^{-1} , immerse seeds: 8 g. kg^{-1}	1200 – 3200
Potato	Blending seeds: 6 g kg^{-1}	2400
Rape	Blending seeds: 5 g kg^{-1}	2000
Ramie	Spray: 100-300 mg L^{-1} (seedling period)	40 – 120
Flax	Blending seeds: 600 g ha^{-1} , spray: appear bud period	600
Reed	Spray: 600-900 g ha^{-1} (seedling or flower period)	600 – 900
Chinese gooseberry	Spray: 700 mg L^{-1} (flower and young fruit period)	280
Haw	Spray: 400 mg L^{-1} (flower period)	160
Banana	Spray: 300-500 mg L^{-1} (seedling and young fruit period)	120 – 200
Astragal	Spray: 300 mg L^{-1} (seedling period)	120
Alfalfa	Blending seeds: 100-300 $\mu g\ g^{-1}$	40 – 120
Mushroom	Spray: 50 mg L^{-1}	20

* assume the amount = 400 L ha^{-1}

REEs in different wastes

The characteristics of waste ashes are mainly dependent on the materials incinerated. The feasibility of applying waste ash to agricultural land will require an evaluation on an individual basis. Extra-application of waste ash to agricultural land can cause phytotoxicity or other adverse effects. However, many previous studies have shown that recycling waste ashes through agricultural soil was practical and did not cause phytotoxicity (Rosen et al., 1994). Waste ashes can also be applied by mixing with other materials such as animal excrement and urine, food scraps, sewage sludge, etc. (Zhang et al., 2001**)**. Concentration of REEs in wastes depends on the kind and source of these wastes. For example, Kawasaki et al. (1998) collected data on REEs and other trace elements in wastewater treatment sludges (Table 2.19). Whereas, Zhang et al. (2001) reported about concentrations of REEs in various waste ashes and the potential risk to Japanese soils (Table 2.20). The results of this study indicated that application of food scrap ashes, animal waste ashes and horticulture waste ashes to agricultural land would cause no REE problem. However, continuous application of sewage sludge ashes or incinerator bottom ashes caused Sc, Sm or Eu accumulation in some Japanese agricultural soils and may be phytotoxic (Zhang et al., 2001).

Table 2.19: Mean REE concentration in sewage sludge, compost, food industry sludge, chemical industry sludge and soils in Japan (adapted from Kawasaki et al., 1998)

Element	Mean REE concentration ($\mu g\ g^{-1}$)				
	Sewage sludge[a]	**Compost[b]**	**Food industry sludge[c]**	**Chemical industry sludge[d]**	**Soil[e]**
La	6.7	2.2	0.9	2.5	17.4
Ce	14.1	3.8	1.8	2.7	35.3
Pr	1.5	0.5	0.2	0.5	4.9
Nd	6.0	2.2	0.9	2.0	22.0
Sm	1.0	0.5	0.2	0.4	4.2
Gd	1.2	0.5	0.2	0.5	4.7
Tb	0.2	0.1	< 0.1	0.1	0.6
Dy	0.9	0.4	0.1	0.3	3.9
Ho	0.2	0.1	< 0.1	0.1	0.7
Er	0.6	0.3	0.1	0.3	2.2
Tm	0.1	0.1	< 0.1	< 0.1	0.3
Yb	0.5	0.4	0.1	0.1	2.1
Lu	0.1	0.1	< 0.1	< 0.1	0.3
Total REEs	33.0	11.0	4.6	9.5	98.9

[a] Sewage sludge was collected from municipal sewage sludge.
[b] Compost made from swine wastes with sawdust.
[c] Food industry sludge collected from wastewater treatment plants in the food industry in Japan.
[d] Chemical industry sludge collected from wastewater treatment plants in the chemical industry in Japan.
[e] The soil, night soil sludge, was from human excreta treatment plants.

Table 2.20: Mean REE concentrations ($\mu g\ g^{-1}$) in various waste ashes (adapted from Zhang et al., 2001)

Element	Food Scrap ashes		Animal waste ashes		Horticulture waste ashes		Sewage sludge ashes		Incinerator bottom ashes	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Sc	5.1	3.2-13.8	8.1	3.3-15.9	12.7	7.1-22.5	19.2	7.1-32.3	6.4	3.8-9.9
Y	8.7	5.1-13.0	10.2	6.3-13.8	17.1	12.0-24.7	16.5	11.6-24.1	15.9	8.6-19.7
La	8.5	7.2-9.8	11.8	9.3-14.5	14.3	11.3-16.8	19.3	14.5-26.3	14.7	6.8-24.4
Ce	15.5	12.5-20	23.5	21.1-29.1	27.3	20.0-33.1	35.4	26.6-43.8	24.6	11.2-41
Pr	1.6	1.1-2.2	3.1	2.3-3.6	3.3	2.6-3.8	3.5	2.2-4.89	2.5	1.1-4.2
Nd	5.9	3.9-8.4	12.2	8.9-15.1	12.9	10.1-14.8	13.7	9.4-19.0	9.3	4.1-16.1
Sm	3.5	1.7-5.1	2.4	1.7-2.8	2.8	2.2-3.6	10.7	8.1-17.9	2.3	0.9-3.8
Eu	0.7	0.2-1.2	0.7	0.5-1.1	0.6	0.5-1.4	1.6	1.1-2.5	1.4	0.3-2.5
Gd	1.3	0.9-1.9	2.9	1.8-4.4	3.1	2.4-3.6	4.1	2.2-6.1	1.9	0.8-3.3
Tb	0.3	0.2-0.4	0.5	0.2-0.7	0.5	0.4-0.6	0.8	0.4-1.2	0.6	0.3-0.9
Dy	0.8	0.5-1.4	2.1	1.2-2.6	2.6	1.9-3.3	2.1	1.3-3.4	1.2	0.5-2.2
Ho	0.1	0.1-0.2	0.4	0.2-0.5	0.5	0.4-0.6	0.4	0.2-0.6	0.2	0.1-0.4
Er	0.4	0.3-0.8	1.1	0.6-1.4	1.5	1.2-2.0	1.1	0.7-1.5	0.7	0.3-1.3
Tm	0.1	0.01-0.1	0.1	0.1-0.2	0.2	0.1-0.3	0.1	0.1-0.2	0.1	0.1-0.2
Yb	0.4	0.3-0.8	1.1	0.6-1.4	1.5	1.2-1.9	1.1	0.7-1.6	0.7	0.3-1.2
Lu	0.1	0.05-0.1	0.1	0.1-0.2	0.2	0.1-0.3	0.1	0.1-0.3	0.1	0.1-0.2
Total REEs	53.7		80.9		101		130		83.1	

2.4 REEs in humans and animals

Under natural conditions, REEs become available, via the groundwater, through leaching from mineral deposits. Certain REEs are detectable at low levels in higher organisms, suggesting that they have some ability to accumulate in food chain, although inhalation is another route to their biological fixation (Figure 2.2). In the latter context, it should be noted that crustal weathering releases REEs into the atmosphere, where their concentrations in aerosols reflect the composition of local rocks (Evans, 1990). Trace amounts of REEs are often detected in mammals, which are listed in Table 2.21. For example, levels of Yb in the eyes of laboratory mice were about 10 times those in other organs (0.23, 0.17, 0.12, 0.30, 0.29 and 2.1 µg g^{-1} for liver, kidney, heart, spleen, brain and total eye, respectively) (Samochocka et al., 1984a and b). The reason for this is obscure, although REEs in the environment may have easier access to the eye than to other organs. However, in mice, the greatest amounts of Yb were associated with the retina and sclera. Lenses of human eyes accumulate La (Swanson and Truesdale, 1971) as age, higher levels being found in cataractous tissue (360 – 490 µg g^{-1} dry wt. for 40 – 55 years). However, Sihvonen (1972) detected no age or sex-related differences between concentrations of various REEs in several human organs (Evans, 1990).

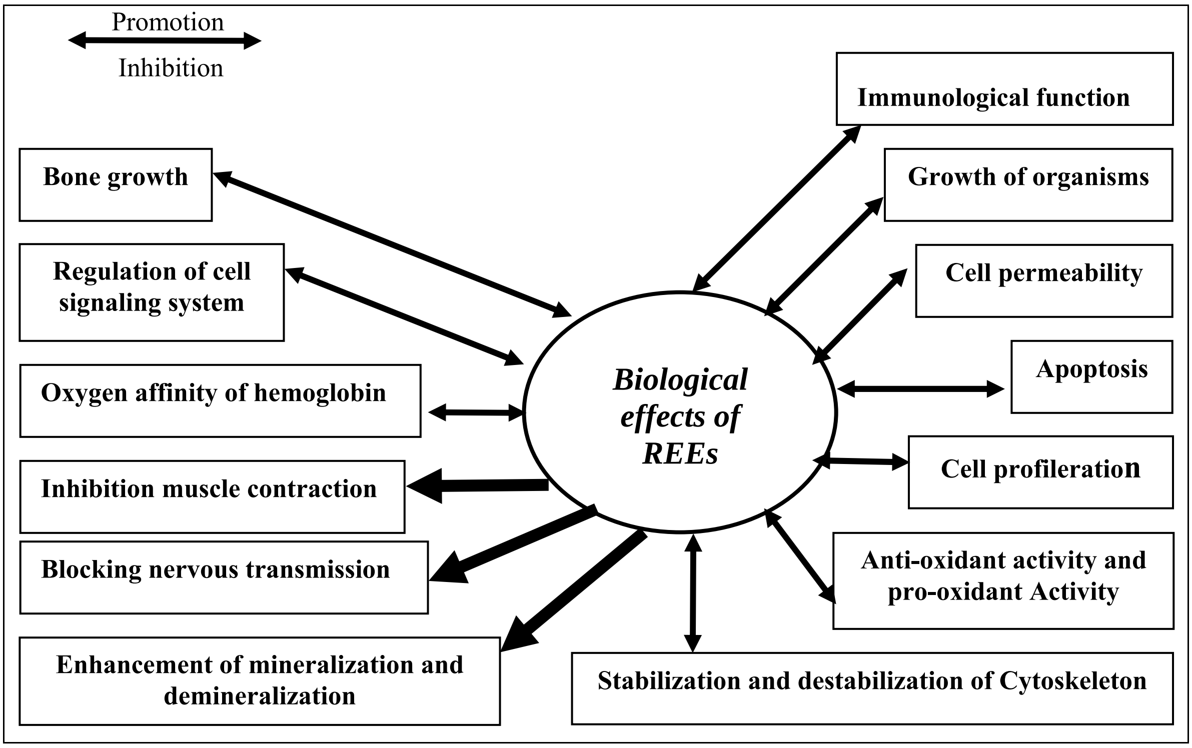


Figure 2.2: Biological effects of REEs (adapted from Wang et al., 2003)

Table 2.21: Concentrations of REEs in organs of different mammals (adapted from Evans, 1990)

Mammal	Organ	REE concentration (ppb)	Reference
Rabbit	Liver, bone, blood	< LLD	Kramsch et al.(1980)
Mouse	Various organs[a]	120- 2,100	Samochocka et al. (1984)
Human	Eye[b]	< LLD - 620,000	Swanson and Truesdale (1971)
	Bone	500	Brooksbank and Leddicotte (1953)
	Kidney	10,300	Leddicotte and Tipton (1958)
	Kidney	0.1	Gerhardsson et al. (1984)
	Spleen[c]	420- 12,400	Erametsa and Sihvonen (1971)
	Heart[d]	< LLD - 2.5	Webster (1965)
	Larynx[e]	0.6- 94.6	Esposito et al. (1986b)
	Lung[f]	0.46- 70.6	Sabbioni et al. (1982)
	Lung[g]	4.5	Gerhardsson et al. (1984)
	Liver	5.5	Sabbioni et al. (1982)
	Lymph nodes[f]	0.7- 106	Sabbioni et al. (1982)
	Blood	< LLD – 45.1	Esposito et al. (1986a)
	Plasma[h]	0.16 – 45.1	Esposito et al. (1986a)
	Synovial fluid[h]	< LLD	Esposito et al. (1986a)
	Urine	< LLD – 2.7	Sabbioni et al. (1982)
	Erythrocyte[i]	4.3	Esposito et al. (1986b)
	Various organs	< LLD – 220,000	Sihvonen (1972)

< LLD – below detection limit. (for more details, see Evans, 1990)
[a] Enriched in eye (various organs of mice).
[b] Increases with age and with cataracts.
[c] Higher values in alcoholics.
[d] Higher values in infarcted tissue.
[e] Lower in malignant tissue.
[f] Higher values in rare earth pneumoconiosis.
[g] Higher values in smelter workers.
[h] Higher values in rheumatoid arthristis and inflammation.
[i] Lower in laryngeal cancer. Increased in inflammation.

REE will be toxic to animals at higher concentrations, but much research has proved that REEs are only slightly toxic to mammals and hardly toxic to *Daphnia carinata* at lower concentrations (Wang et al., 2003e). Current questions pertinent to the food chain are: (1) whether the REEs can enter the human body and affect physiological functions on the cellular level; and (2) what is the toxicity threshold of humans and other mammals. According to Evans (1990), REEs are not transportable across the biomembrane into the cell. In a study on tetrahymena (Liu et al., 1984), it was found that REEs could enhance the growth and segmentation at low concentration (5–20 μg g^{-1}). This phenomenon is much like that of the toxic elements such as Hg, Cd, and Tl (Wu et al., 2002).

3 Material and Methods

3.1 Soil Characteristics

The soil used in the experiment (0 – 25 cm) was collected from the experimental field (10° 22′ E, 52° 18′ N, 81 m above sea level) of the Federal Agricultural Research Centre for Cultivated Crops (JKI, Institute for Crop and Soil Science, former FAL). The soil was composed of 46% sand, 47% silt, and 7% clay; hence, it is characterized as strong silty sand following the German classification system (AG Boden, 1994) or loam according to USDA classification. Table 3.1 shows some chemical, physical and microbial characteristics of the soil used in the experiment. The soil was air-dried and sieved to particle size 2 mm. For microbial investigation the soil was stored in plastic bags provided with a cotton stoppers to enable gas exchange. The individual REEs (total and available content), soil moisture content (PW), water holding capacity (WHC), copper (total and available content), calcium (total and available content) in the used soil and the Chinese REE fertilizer were analyzed before starting the experiment.

Table 3.1: Selected some chemical, physical and microbial characteristics of the soil used in experimentation

Element or parameter		
Chemical soil properties or analysis		
	Total (µg g^{-1}) using (*Agua Regia*)	Available (µg g^{-1}) using Sillanpää (1982) method
La	12.5	1.0
Ce	26.3	0.8
Nd	10.7	0.7
Pr	2.8	0.2
Cu	9.8	4.3
Ca	1420	983
Soil EC	109 (mS m^{-1})	
Soil pH	5.2	
Physical soil analysis		
Soil texture	Silty sand (AG Boden, 1994) or loam according to USDA classification	
Silt	47%	
Clay	7%	
Sand	46%	
Water Holding Capacity (WHC)	35%	
Microbial soil assessments		
Microbial counts (CFU)		
Bacteria	4187788 (4.1×10^6)	
Actinocycetes	139636 (1.3×10^5)	
Fungi	14172 (1.4×10^4)	
Dehydrogenase Activity (DHA)	53.5 (µg TPF* g^{-1} DM d^{-1})	
Alkaline Phosphatase Activity (AlP)	191 (µg p-NP** g^{-1})	

* TPF, Triphenylformazan

** p-NP, p-nitrophenol

3.2 Experimental Design

The effect of REE on agricultural crops was tested in a pot experiment in the greenhouse. Two agricultural crops were tested:

- Maize (*Zea mays* L.) variety "Magister".
- Oilseed rape (*Brassica napus* L.) variety "Licosmos".

The pot experiment has been conducted in the greenhouse under controlled conditions; the total water holding capacity (WHC) was controlled by adding water to 60% of WHC during the experimental period. The pots (capacity 1 litre) contained 900 g of soil substrate (dry weight basis) and were seeded with 6 maize seeds and 10 oilseed rape seeds on April 29th and Mai 14th and harvested on July 5th and July 17th in 2005 and 2006, respectively (Figure 3.1). The total amount of the essential nutrients which were applied to maize and oilseed rape are listed in Table 3.2.

Table 3.2: Rates (µg g^{-1} dry soil) of essential nutrients which were added to both maize and oil seed oilseed rape

Element or nutrient	Chemical formula	Maize		Oilseed rape	
N	NH_4NO_3	1000	(2 rates)	1000	(2 rates)
P	$Ca(H_2PO_4)_2 \times 2H_2O$	100	(1 rate*)	100	(1 rate)
Mg	$MgCl_2 \times 6H_2O$	50	(1 rate)	50	(1 rate)
S	K_2SO_4	150	(1 rate)	250	(1 rate)
K	KCl	243 mg			

* First rate before sowing, second rate after thinning. The K rate was added to balance for maize and oilseed rape

The essential nutrients were mixed homogenously with the soil before cultivation. Seeds were cultivated at a depth of 0.5 cm and 1.0 cm for oilseed rape and maize, respectively. REEs were applied at rates being multiples of the plant available content in soils (Table 3.3). The plant available REE content in the soil was determined annually before the experimentation started and rates adapted accordingly.

After emergence, the seedlings were thinned in each pot to 4 and 3 seedlings for oilseed rape and maize, respectively. At thinning, 8 leaf discs were taken from each crop to determine stress related enzyme activities in plant leaf discs (see section plant analyses). Each treatment combination was carried out with 4 replicates. The experiment was carried out with vegetated and non-vegetated soil. Plants were grown for about 9 weeks. During this time, the pots were watered daily with deionized water to 60% of WHC to warrant an optimal water supply for the growing plants.

Growth stages were determined according to the BBCH code (Meier et al., 2001). At harvest, maize plants were at BBCH 17/32 (between 6 and 8 leaves), and oilseed rape plants were at BBCH 32 (between 6 and 8 leaves).

Table 3.3: REE application rates in green house experimentation

Element/fertilizer		Calculation base	Rate (µg g^{-1})		Chemical formula
			2005	2006	
		Control	0	0	
REE-fertilizer	REE1	Plant available content (PAC)	2.7	2.7	$RECl_3 \times xH_2O$
	REE2	10 fold PAC*	27	27	
	REE3	50 fold PAC	135	135	
	REE4	100 fold PAC	270	270	
Lanthanum	La1	Plant available content (PAC)	1	1	$LaCl_3 \times 7H_2O$
	La2	10 fold PAC	10	10	
	La3	50 fold PAC	50	50	
	La4	100 fold PAC	100	100	
Cerium	Ce1	Plant available content (PAC)	0.8	0.8	$CeCl_3 \times 7H_2O$
	Ce2	10 fold PAC	8.0	8.0	
	Ce3	50 fold PAC	40	40	
	Ce4	100 fold PAC	80	80	
Calcium	Ca1	1% from PAC	9.83	1	$CaCl_2 \times 2H_2O$
	Ca2	10% from PAC	98.3	10	
	Ca3	50% from PAC	491.5	50	
	Ca4	100 % from PAC	983	100	
Copper	Cu1	Plant available content (PAC)	4.3		$CuCl_2 \times 2H_2O$
	Cu2	10 fold PAC	43		
	Cu3	50 fold PAC	215		
	Cu4	100 fold PAC	430		

* PAC= Plant Available Content

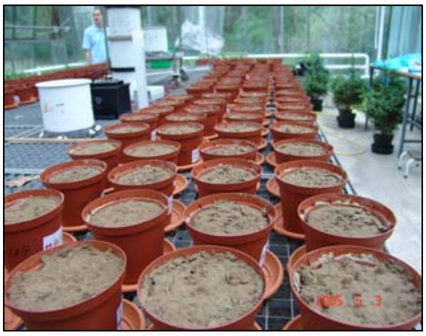
At harvest, shoots and roots were collected separately and the fresh weight was determined. Leaf discs were taken from each crop to determine stress related enzyme activities in plant leaf discs. Roots were stored in a refrigerator at –20 °C before further performance. Then, roots were washed with deionized water and dried at 65 °C until constancy of weight. The dry weight of roots was measured. Shoots were oven-dried at 65 °C until constancy of weight, fresh and dry weights were determined. The dry plant material was ground and kept in sealed PE-containers until chemical analysis. The soil in the pots (about 200 g) was sieved at 2 mm mesh size and stored at 4 °C in small plastic bags closed with cotton plugs to guarantee aerobic conditions until microbial assessments were made. The remaining soil in the pots was dried at room temperature and the air dried soil was sieved at < 2 mm and stored.

3.3 Analytical Methods

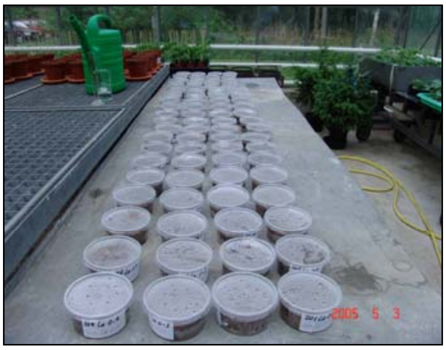
Determination of the plant available REE content in soil

The method of Sillanpää (1982) was used to determine the plant available REE content: Ammonium acetate EDTA extraction solution (0.5 M CH_3COONH_4, 0.5 M CH_3COOH and 0.02 M Na_2 EDTA) was diluted as follows: 571 ml 100% CH_3COOH, 373 ml 25% NH_4OH and 74.4 g Na_2 EDTA to 10 L with deionized water. The pH was adjusted to 4.65 with acetic acid or ammonium hydroxide. Then, 5 g of soil and 50 ml extracting solution were shaken in PE-bottles for 1 hour in an end-over-end shaker with 27 r.p.m. The suspension was filtered using Schleicher and Schuell (593 1/2) paper filters.

Soil collection

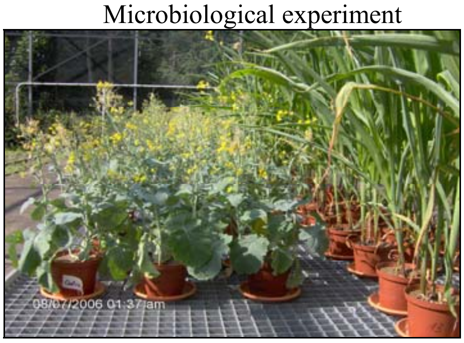


Emergence stage



Microbiological experiment

Vegetative growth stage



Oilseed rape at flowering (BBCH)

Soil preparation

Storage of soils in plastic bag at 4°C
for microbial assessments

storage of soil samples
for soil chemical analysis

Figure 3.1: Some experimental performance stages (for more details see Appendix)

For ICP analysis, 50 mL of the extraction solution was evaporated in a crucible to dryness on a sand bath adjusted to 170 °C. For ashing of the residue, the crucible was heated in a muffle furnace (500 °C) over 5 hours. The ash was solved with 10 mL 10% HNO_3 in the crucible by means of stirring with a teflon rod and filtered with deionized water into 25 mL measuring flask.

The Chinese REE fertilizer was provided by the National Rare Earth Centre for Agriculture (Grirem Advanced Materials Co., Ltd., Beijing, China). The water-soluble REE content of Chinese REE fertilizer was determined (Table 3.4). 1 g Chinese fertilizer was dissolved in 50 ml deionized water and filtered using filter paper (Schleicher and Schuell, 593 1/2) and then analyzed by ICP-MS.

Table 3.4: The composition of Chinese REE fertilizer ($RECl_3 \times xH_2O$)

Chinese REE Fertilizer analysis	
Approved total REE content (%)	**Water soluble REE content (%)**
$La_2O_3 > 32$	La = 7.78 La_2O_3
$Ce_2O_3 > 61$	Ce = 14.11 Ce_2O_3
$Pr_6O_{11} > 6.5$	Pr = 1.39 Pr_6O_{11}
$Nd_2O_3 > 0.5$	Nd = 4.72 Nd_2O_3
	Total REEs (only La, Ce, Pr, and Nd) = 2.7 µg REE g^{-1} fertilizer.

Microbial Counts

Actinomycetes were enumerated using the method following Drews (1983). Fungi were determined with “Wuerze-Bouillon” (Merck) 50% concentrated, amended with 0.03 mg rose Bengal and solidified by 20 g L^{-1} agar–agar. The number of heterotrophic aerobic bacteria, actinomycetes and fungi was determined by the spread plate technique according to Stöven (1999). The method can be divided into the following stages:

1. Extraction

Microorganisms were aseptically collected in 90 mL of a sterile 0.1% Napp (tetrasodium pyrophosphate, $Na_4P_2O_7 \times 10H_2O$, 1 g L^{-1} dissolved in deionized water and pH was adjusted to 7). 10 g of fresh soil and 90 ml of Napp solution were placed in a 200 ml SCHOTTGLAS bottle. 5 glass beads (Ø 3 mm, sterilized) were added. This represented the extract (dilution of 10^{-1}). The samples were shaken for 20 min. at 200 r.p.m at room temperature. Coarse particles settled after 10 min. The supernatant was diluted with 9 ml physiological sodium chloride (0.9% NaCl, i.e., 9 g NaCl in 1 L deionized water) in case of bacteria and fungi. For actinomycetes, it was diluted with 9 ml phenol (1 g dissolved in 140 ml deionized water). From dilution of 10^{-1}, the following dilutions were made by taking 1 ml from dilution 10^{-1} to the following one (10^{-2}), then again 1 mL from dilution of 10^{-2} to the following one (10^{-3}) and so on. Before taking 1 ml from each test tube, the test tubes were shaken. The dilutions were 10^{-2}, 10^{-3}, and 10^{-4} for fungi and actinomycetes and 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6} and sometimes up to 10^{-9} for bacteria (Figure 3.2). After all test tubes were prepared, they were put in the test tubes stand. 0.1 mL was taken by micro-pipette and put in Petri dishes which contained the medium. Afterwards, the solution was spread homogenously by spatula in Petri dishes. Each 4 replicates (dishes) were placed vertically and the inoculation of Petri dishes began from bottom to top.

2. Dilution

A serial dilution was carried out; 1 mL of supernatant was added at 9 ml of 0.9 % NaCl for the 10^{-2} dilution, 1 ml of dilution 10^{-2} was added at 9 ml of 0.9 % NaCl for the 10^{-3} dilution etc. The following dilutions were employed:

- Fungi: 10^{-2}, 10^{-3}, and 10^{-4} and up to 10^{-5}.
- Aerobic heterotrophic bacteria: 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6} and up to 10^{-9}
- Actinomycetes: 10^{-2}, 10^{-3}, and 10^{-4} and up to 10^{-5}.

3. Inoculation

The spread plate technique was used for enumerating microorganisms (Stöven, 1999). So, after preparing the dilution series, the spread plate technique was prepared as follows:

1. 0.1 mL from serial dilutions was dropped onto the surface of an agar plate.

2. Inoculum was spread across the surface using a sterilized spreader. By spreading the suspension over the plate, a dilution gradient was established to provide isolated colonies.

3. Incubated agar plates inverted in appropriate conditions. Fungi and bacteria were inoculated for 7 days in the dark at 20 °C ±2 °C, actinomycetes for 14 days at the same temperature.

4. Counting colonies and calculation of the number of microorganisms in the original suspension was carried out.

4. Evaluation

Determination the microbial colony forming units per grams of dry soil was calculated using the following equation:

$$\mathbf{CFU = N \times C \times 10\ (100\ /100\ -\ \%\ M)}$$

CFU = Colony Forming Unit (CFU g^{-1} dry soil).
N = Mean of the count of colonies of 4 agar plates of the same dilution.
C = Concentration of the used dilution.
100 / 100 – % M = Conversion factor to express in dry soil.
10 = dilution factor.
(% M) = Percentage moisture in the soil.

Bacteria

For the determination of the populations of heterotrophic aerobic bacteria 50% concentrated “Standard I – nutrient broth” (Merck, Darmstadt, Germany) was used and solidified by 20 g L^{-1} agar-agar. 2.5 g Standard I was dissolved in 975 g deionized. The pH was adjusted to 7.5 (with 2N NaOH or 2N HCl). After that, 15 g agar–agar was added, magnetic stirrer was put and the solution was stirred for 5 min. The nutrient solution was sterilized in an autoclave for 15 min. at 121 °C and 100 kPa. After cooling to about 50 °C the solution was placed in Petri dishes.

Fungi

16.5 g wort broth (Tables 3.5 and 3.6) were dissolved in 962.5 g deionized water and the pH was adjusted to 4.5. After that, 20 g agar–agar was added. The medium was sterilized in an autoclave (FVA2/3, IBS Integra, Fedegari Autoclave, Italy) for 15 min. at 121 °C and 100 kPa. Exactly 1 mL Rose Bengal (covered with aluminum paper to prevent light) was added to the sterilized solution and stirred for a few minutes to make the solution homogeneous and red coloured. Afterwards, the solution was cooled down to about 50 °C and placed in Petri dishes.

Table 3.5: Composition of fungi, bacteria and actinomycetes media

Fungi		**Bacteria**		**Actinomycetes**	
Ingredients	Amount	Ingredients	Amount (g)	Ingredients	Amount (g)
Wort broth*	16.5 g	Standard I Broth*	2.5	Glucose	2.0
				Casein	0.2
				KH_2PO_4	0.5
				$MgSO_4 \times 7H_2O$	0.2
				Trace element solution*	5 mL
Deionized water	962.5 g	Deionized water	975	Deionized water	975
pH	4.5 g	pH	7.5	pH	6.7
Agar-agar	20 g	Agar-agar	15	Agar-agar	15
Rose Bengal (0.03 mg mL^{-1})	1 mL				

* For more details about the composition of worth broth, standard I and trace element solution see Table 3.6.

Table 3.6: Chemical composition of wort broth, Standard I and trace element solution

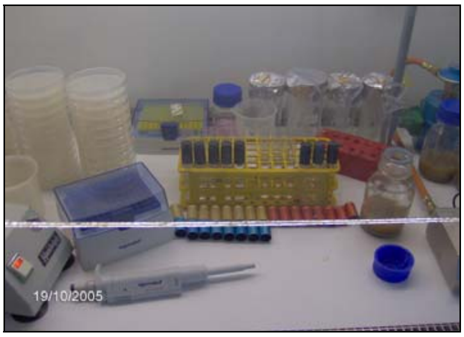
Trace element solution (Drews, 1983)		**Wort broth (Merck)**		**Standard I Broth (Merck)**	
Ingredients	Amount (mg)	Ingredients	Amount (g)	Ingredients	Amount (g)
EDTA	500	Malt extract	7.5	Peptone	7.5
$FeSO_4 \times 7H_2O$	300	Universal peptone	0.375	Yeast extract	1.5
$MnCl_2 \times 4H_2O$	3	Maltose	6.375	NaCl	3.0
$CoCl_2 \times 6H_2O$	5	Dextran	1.375	D (+) glucose	0.5
$CuCl_2 \times 2H_2O$	1	KH_2PO_4	0.375		
$NiCl_2 \times 6H_2O$	2	NH_4Cl	0.5		
$Na_2MoO_4 \times 4H_2O$	3				
$ZnSO_4 \times 7H_2O$	5				
H_3BO_3	2				

Actinomycetes

2.0 g glucose and other components (Casein, KH_2PO_4, $MgSO_4 \times 7H_2O$ trace element solution and deionized water) were prepared as shown in Tables (3.5) and (3.6), the pH was adjusted to 6.7 and then, 15 g agar-agar was added. After that, the medium was sterilized in the autoclave for 15 min. at 121 °C and 100 kPa. 2 ml DMSO (dimethyl sulfoxide) kept in a test tube was sterilized also. After the sterilization, 0.1 g Nystatin was solved therein. This solution was mixed with the liquid agar medium after cooling down to 50 °C. Additional 0.05 g actidion was added. Afterwards, the medium was placed in Petri dishes.

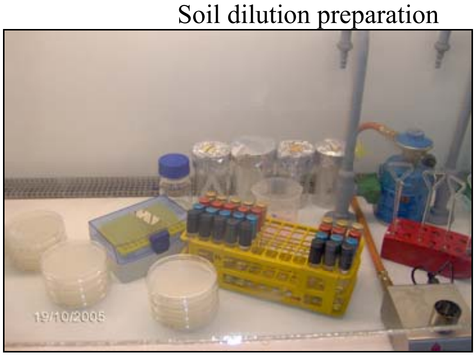
Test tube preparation

Soil extraction preparation



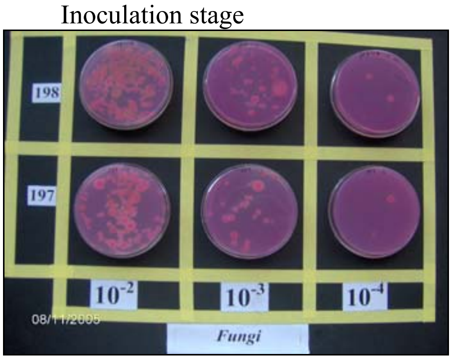
Soil dilution preparation

Agar plate preparation



Inoculation stage

Storing at 20 °C under exclusion of light



Microbial (fungi) counting

Sterilization in plastic bags

Figure 3.2: Some relevant stages for counting soil microbial numbers (for more details see Appendix)

In order to prevent contamination with fungi and especially yeast, nystatin was used. To avoid vegetative bacteria growth dilution series were prepared with phenol (1 g phenol dissolved in 140 ml deionized water). In this condition only is expected to find arthospore, which are the spore of actinomycetes that was being before counting of the actinomycetes. Count only colonies which are colored (red, brown, yellow etc.)

Enzymatic assessments in soil

Measurements of several enzymatic activities have been used to establish indices of soil fertility (Beck, 1984; Stefanic et al., 1984; Pascual et al., 2000). Enzymes are produced by microorganisms and plants, and in the soil they act as biological catalysts of important reactions to produce essential compounds for both soil microorganisms and plants. Assays of soil enzymatic activities include all enzymatic forms present in the soil (Nannipieri, 1994). They also determine the potential enzymatic activity of a soil under optimum conditions of moisture, pH, temperature and substrate concentration. Enzymatic activities may vary under stress, for instance when the soil is contaminated by heavy metals (Moreno et al., 2003).

Dehydrogenase activity

Dehydrogenase is an enzyme that oxidizes a substrate by transferring hydrogen to an acceptor, usually NAD/NADP or a flavin coenzyme. In addition, it catalyzes the removal of hydrogen from a substrate and the transfer of the hydrogen to an acceptor in redox reaction. It reflects a broad range of oxidative activities and dehydrogenase is an intracellular enzyme which measurement free dehydrogenase does not exist in soil.

The dehydrogenase activity is measured according to the method of Thalmann (1968), modified by Malkomes (1991). The used reagents are light sensitive.

<u>Solutions</u>

Tris buffer (0.1 M)

12.1 g Tris (hydroxymethyl) aminomethane was dissolved in 600 mL deionized water using about 25 mL HCl 10% (from concentrated acid 37%) and the pH was adjusted to 7.6. Finally, the solution was completed to 1000 mL.

Substrate solution (0.5%)

0.5 g TTC (2,3,5 – Triphenyltetrazolium chloride) was dissolved in 100 mL Tris buffer and the solution stored in the dark at 4 °C.

TPF – stock solution (10 mg mL^{-1})

0.2 g TPF (Triphenylformazan) is dissolves in 20 mL acetone and the solution was stored in the dark at 4 °C.

TPF – solution (100 µg mL^{-1})

0.1 mL TPF stock solution was added to 9.9 ml acetone. TTC and TPF solutions are very sensitive to light. The solutions should store in bottles and cover with aluminum paper.

Calculations

To determine the µg TPF in the filtrates from the calibration curve, the following equation was used:

$$\mathbf{TPF = (S - C) \times 100 / (2 \times \%DM)}$$

TPF = Triphenylformazan [µg g^{-1} DM d^{-1}]
S = extinction value, µg TPF (average of replications) estimated on the base of the calibration curve.
C = control, it was also calculated on the base of calibration curve mentioned before (µg TPF)
2 = initial soil weight (g);
100 / % DM = factor for soil dry matter.

Alkaline phosphatase activity

Alkaline phosphatase (ALP) is a hydrolase enzyme responsible for removing phosphate groups in the 5- and 3- positions from many types of molecules, including nucleotides, proteins, and alkaloids. The process of removing the phosphate group is called dephosphorylation. As the name suggests, alkaline phosphatases are most effective in an alkaline environment. Alkaline phosphatase is only produced by micro-organisms. Alkaline phosphatase activity is often increased in the rhizosphere compared to the bulk soil (Tarafdar and Claassen, 1988).

The alkaline phosphatase activity was measured according to Tabatabai (1982). For measuring the alkaline phosphatase, 1 g fresh (field-moist) soil was weighed and put into four Erlenmeyer flasks. Just 1 mL of substrate solution and 4 mL of the corresponding working buffer solution were added to three flasks (samples) and 4 mL of working buffer solution was added with micro-pipette into the fourth flask (control). All flasks were shaken briefly for few minutes and incubated for 1 h at 37 °C in the dark. After incubation, 1 mL of the substrate solution was added to the control. Subsequently all samples received 1 mL calcium chloride solution, 4 mL NaOH solution and 10 mL deionized water were added and shaken briefly. For filtration, Whatman paper (595 ½) were used. The extinction of the yellow color intensity of calibration standards' samples and controls was measured with a spectrophotometer at 400 nm against the reagent blank.

Solutions

Modified universal buffer stock solution (MUB)

12.1 g of Tris (hydroxymethyl) aminomethane was dissolved with 11.6 g of maleic acid, 14 g of citric acid monohydrate, 6.3 g of boric acid, 488 mL NaOH (1 M) and the solution was completed to 1000 mL with deionized water in a volumetric flask.

Working buffer solution

200 mL of modified universal buffer stock solution was mixed and 500 mL of deionized water and the pH were adjusted to 11 with NaOH. Afterwards, the volume was adjusted to 1000 mL with deionized water in a volumetric flask.

Calcium chloride (0.5 M)

36.74 g of $CaCl_2 \times 2H_2O$ was dissolved in deionized water and the volume was diluted to 500 mL with deionized water in volumetric flask.

Sodium hydroxide (0.5 M)

20 g of NaOH was dissolved in deionized water and the volume was diluted to 1000 mL with deionized water in volumetric flask.

Standard stock solution (1 mg p-nitrophenol mL^{-1})

1.0 g of p-nitrophenol in was dissolved in deionized water and the volume was diluted to 1000 mL with deionized water in volumetric flask.

Substrate solution:

0.464 g of disodium p-nitrophenyl phosphate hexadydrate (Merck 6850) was dissolved in working buffer solution and diluted with 50 mL of working buffer solution in volumetric flask. Soil samples were analyzed photometrically using a spectrophotometer (Specorol 50, Analytikajena AG, Germany).

Calculations

To determine the µg p-nitrophenol (p-NP) per gram dry matter for the incubation time in the filtrates from the calibration curve, the following equation was used:

$$\boxed{\textbf{p-NP} = (S - C) \times 10 \times 100 \times [DM\ (\%)]^{-1}}$$

p-NP = µg p-nitrophenol g^{-1} dm^{-1} h^{-1}
S = mean value of sample (µg p-NP).
C = mean value of control (µg p-NP).
10 = dilution factor.
$100 \times [DM\ (\%)]^{-1}$ = factor for soil dry matter.

Stress related enzyme activities in plant leaf discs

Stress situations cause increased production of toxic oxygen derivatives. To counteract the toxicity of active oxygen species, a complex antioxidative defense system, composed of both non-enzymic and enzymic constituents, is present in all plant cells (Foyer et al., 1994). In response to the increased production of oxygen radicals the capacity of the antioxidant defense system is increased but in most situations the response is moderate (Rios-Gonzalez et al., 2002).

The most important antioxidative enzymes are catalase (CAT), peroxidases (POD), superoxide dismutase (SOD), and those of the ascorbate–glutathione cycle, a series of coupled redox reactions involving four enzymes: ascorbate peroxidase (APX), monodehydroascorbate reductase (MDHAR), dehydroascorbate reductase (DHAR), and glutathione reductase (GR). The main non-enzymatic antioxidant molecules are ascorbate, glutathione, ß-carotene, and flavonoids (Palma et al., 2006).

To determine stress related enzyme activities in plant leaf, 8 leaf discs (diameter 1 cm) from the middle of leaf blade were taken from each crop. The leaf discs immediately put in liquid N_2 and transported to the laboratory and then stored in a freezer (PowerFreezer^{TM}, Deep Freezer, Juan, VXS 380/490/570/600, France) at – 80 °C (Figure 3.3). All analyses of the leaf discs were carried out in Graz University (Austria) by Prof. Dr. Dieter Grill and Dr. Karin Herbinger (Institute of Plant Physiology).

α-Tocopherol (Vitamin E)

α-Tocopherol was determined according to a method described by Wildi and Luetz (1996), which is slightly modified. Acetone extracts (prepared in the same way as the pigment extracts, see above) are subjected to isocratic HPLC analyses. HPLC hardware: ChromSun HPLC SunFlow 100 pump. Hitachi Fluorescence Spectrometer F-1300 (excitation: 295 nm, emission: 325 nm), Midas Spark Holland autosampler cooled at 4 °C, Chrom Spherisorb S5 ODS-2 250 x 4.6 mm column with Chrom Spherisorb S5 ODS-2 10 x 4.6 mm precolumn, solvent: methanol, run time: 30 minutes, flow rate: 1 mL min^{-1}. Calibration is done by calibration curves of acetone solutions of commercial tocopherol standards.

Total chlorophyll

Total chlorophyll of leaf discs was determined according to Pfeifhofer (1989).

Leaf discs cutting   Leaf discs in aluminium paper


Leaf discs in a freezer at -80 °C   drying of leaf discs

Figure 3.3: Leaf discs performance stages (for more details see Appendix)

Physical soil analyses

Maximum water holding capacity (WHC_{max})

The maximum water holding capacity was determined according to Stöven (1999). It was measured using cylinder of glass (7.5 cm height and 3.6 cm inner diameter), funnel, beaker, and a piece of moist cloth. The cylinder was put in the beaker. One of the two ends of cylinder was tied with a piece of moist cloth and with funnel at least 35 g fresh soil was put within funnel into the cylinder. Afterwards, water was put into the beaker surrounding cylinder (the water level should be as high as the soil column in the cylinder). After that, cylinder was covered with watch glass for 120 min. The supply of water was continued more 30 min. between cylinder and beaker. After that, bath of sand in suitable container was prepared and was saturated with water. Subsequently, the cylinder was transported vertically at the sand bath and left it 120 min. with covering. Afterwards, the soil cylinder was taken and put into a new and clean beaker. The collected soil in new cylinder was weighed and put in oven at 105 °C for 24 hours. After drying the soil was weighed and its weight express about water holding capacity.

The measured water content corresponds to the maximum water-holding capacity (WHC) of the soil under laboratory conditions; it is expressed as g water per 100 g dm using the following equation:

$$\mathbf{WHC_{max}}\ (\%) = [(\text{saturated soil (g)} - \text{dried soil (g)}] \times 100 / \text{dried soil (g)}$$

Soil moisture content (PW)

The soil moisture content was determined in all pots after finishing the experiment by Kern apparatus (model MLB – 50E, Germany). The measuring is beginning with turn on the instrument for 5 min. to warm. After that, the aluminum dish was weighed and press tare. The fresh soil was put in the aluminum dish (at least 3 g and not more than 20 g soil). After pressing start twice, the heating of the apparatus is being to evaporate soil moisture. After the alarm, the reading of the instrument was the moisture content in the used soil as percentage (dry weight base).

Chemical soil analyses

Determination of REEs and other mineral in soil

All chemical analytical methods were carried out on air-dried soil samples. The total REE content in soils was detemined by using *aqua regia* digestion and NH_4AcEDTA extraction. Ca and Cu were determined in the same extract. For the final determination of REEs Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) was used, for Ca and Cu Atomic Absorption Spectroscopy (AAS).

Soil pH

The soil samples were weighed (20 g fresh soil) and put in 250 ml SCHOTTGLAS. 50 mL deionized water was added into the glass and was shaken for 60 min. at a horizontal shaker at 200 r.p.m. Afterwards, the soil pH was determined using a pH meter [pH 525, Wissenschatlich Technische Werkstaette (WTW), GmbH, Germany] (Hoffmann, 1991).

Soil salinity (EC)

After determination of the soil pH, the soil suspension was filtrated at 20 °C (the temperature of the measuring room was 20 °C). Then, the filtrates were measured using an EC instrument [LF 521, Wissenschatlich Technische Werkstaette (WTW), GmbH, Germany].

Plant analyses

At harvest, plants were cut about 1.5 cm above the soil surface. The roots were extracted separately from the soil. The harvested plant materials were washed with deionized water then dried employing fresh air at 65 °C until constancy of weight. The dried plant material was fine ground using a Retsch mill (RETSCH, TYP PS-1, Haan, Germany). The dry matter yield of shoots and roots of maize and oilseed rape were determined. The plant material was digested by employing a microwave (CEM Mars Xpress, GmbH, Germany). The following extraction procedure was applied:

0.5 g ground plant material was weighed in microwave tubes. 6.0 mL HNO_3 (65%

concentration) and 1.5 mL H_2O_2 (30% concentration) were added with a micro-pipette to each sample. All microwave tubes were completely closed and the microwave program started for plant samples. The program was as follows:

I. 5 minutes for raising the temperature to 120 °C; 2 min. at 120 °C.

II. 5 minutes for raising the temperature to 200 °C; 15 min. at 200 °C.

III. 30 minutes for cooling.

After the program ended, the tubes were cooled. Using gloves, the digested materials in tubes were filled in flasks (50 mL) and filtrated with filter paper (Schleicher & Schuell, 593 ½). The filtered solution was transferred in plastic PE-bottles. The digested solution was used for chemical analysis of elements. The REEs (La, Ce, Pr and Nd) were determined using ICP-QMS (PlasmaQuad, UK). Fe, Mn, Zn, Mg and Cu were determined using atomic absorption spectroscopy (AAS) [UNICAM 929, AA Spectrometer, UK]. K and Ca were measured by flame photometer (Eppendorf –D, ELEX 6361, Germany) and S and B using ICP-OES (SpectroFlame M120 S, Germany) (see Appendix).

3.4 Statistical Analysis

The results were analyzed statistically by a General Linear Model procedure and 2 way analysis of variance (ANOVA) using the Statistical Package for Social Sciences (SPSS) version 12.0 (SPSS, 2003). Mean separation procedure was performed using Tukey's test at a 0.05 level of significance. Correlation and regression analysis were used to determine the relations between the factors. All calculations were made on a dry weight basis.

4 Results

The main objectives of the present study were to determine the dose/effect relationships of graded REE applications on soil microbiological parameters (soil enzyme activities and microbial counts) using maize and oilseed rape as test crops in order to contribute to a better understanding of the environmental chemistry of REEs. In addition, dose/effect relationships of graded REE applications on uptake and growth parameters of maize and oilseed rape crops (yield parameters and uptake of minerals) were determined. Such investigations are required for instance for ecotoxicological risks assessments of REEs in the environment.

In the past years, REE-fertilizers have been widely used in the crop and forest agriculture, livestock breeding, aquiculture etc. in China and other countries (Hu et al., 2004). In 2005, China's usage of REE-fertilizers in agriculture was as high as 51,900 tons though these products have not been officially approved yet. With the increase in the usage of REE-fertilizers in agriculture, REEs would inevitably enter the rural environment and carry-over in the food chain might affect human welfare (Weltje et al., 2002). Thus, REEs may influence food safety and human health. For example, it has been reported that the mean intelligence quotient and memory of children in areas with high background concentrations of REEs are significantly lower than those in control areas (Zhu et al., 1996). REEs have already been classified as the main environmental pollutants in China since the1990s (National Natural Science Foundation of China 1996; Ye et al., 2007).

The ability of REEs, mainly lanthanides, to substitute for a large number of metallic ions, such as Ca^{2+}, Mg^{2+}, Fe^{3+} or Mn^{2+}, plays a major role in biochemical behavior of these elements (Evans, 1983). Among these metallic ions, Ca^{2+} is of particular interest. Given the importance of Ca in cellular metabolism and the efficient displacement by lanthanides, a high biological activity of lanthanide ions is expected. Yet their inability to normally penetrate the cellular membrane of living cells restricts their biological activity (Evans, 1983). Marked similarities in size, bonding but also in coordination geometry and donor atom preference enables them to replace Ca^{2+} specifically in various physiological processes. Even through occurring isomorophously, the substitution of Ca^{2+} in enzymes and other molecules is not necessarily associated with a loss in functionality (Evans, 1990). REEs have been shown to activate a number of proteins and enzymes, while in other cases they inhibited Ca^{2+} and Mg^{2+} functions (Redling, 2006).

REEs have similar characteristics as Ca. REEs have a mean ionic radius of 9.6-11.5 nm compared to Ca with ion 9.9 nm. Consequently, many chemical characteristics of REEs have the same binding sites in organisms as Ca, and thus show similar effects on plant metabolism (Hu et al., 2004). The effects of REEs on physiological functions of Ca in plants have been summarized by Brown et al., (1990). They have concluded that:

- REEs have similar functions as Ca, especially La, which therefore was nicknamed "super-calcium."
- The activity of many enzymes and other functional-proteins was inhibited by La^{3+}.

La^{3+} can displace Ca^{2+} from extra-cellular binding sites and can inhibit the efflux of extra-cellular, and part of the intracellular Ca^{2+}.

Even though Ca^{2+} and La^{3+} ions are reported to be quite similar, two major differences have been documented. Firstly, REE ions display a much higher charge-to-volume ratio which, in turn leads to increased stability of lanthanide complexes (Jakupec et al., 2005). The second reason is the ligand exchange rate. Water molecules exchange about 10 times faster around the Ca^{2+} ion. This is presumably due to the higher charge-to-volume ratio of the REE^{3+} ions which probably lowers of the off-rate of complex dissociation (Evans, 1990).

In the present investigation an essential nutrient and direct counterpart of REEs (Ca) and a heavy metal, copper (Cu) was selected for experimentation in order to assess comparative plant toxicological effects of REEs. In plants, Cu plays a vital role in photosynthesis and respiratory electron transport where it functions as a cofactor for a variety of enzymes such as superoxide dismutase, cytochrome *c*, oxidase and plastocyanin (Clemens, 2001). However, excessive levels of Cu can cause a range of morphological and physiological disorders (Fernandes and Henriques, 1991) such as reduction of growth (Zheng et al., 2005), photosynthetic activity (Burzynski and Klobus, 2004), and uptake of mineral nutrients (Wang et al., 2004). Moreover, it may result in chlorosis, inhibition of root growth, and damage to plasma membrane permeability that leads to ion leakage (Ouzounidou et al., 1992). For most crop species, the typical Cu concentration in plant tissues is 5–20 $\mu g\ g^{-1}$, and above this upper limit, toxicity effects are likely to occur (Rouphael et al., 2008). Excess concentrations of Cu are said to generate oxidative stress due to an increase in the levels of reactive oxygen species (ROS) within sub-cellular compartments (Mittler et al., 2004). Toxic effects of Cu on plants were reflected by reductions in fresh weight (FW), shoot and root length, chlorophyll and carotenoids contents (Khatun et al., 2007).

Next to the response to REEs (La, Ce, and REE-fertilizer) and Cu that of increased applications of Ca were tested. The application rates of REE, Cu and Ca were multiples of their plant available concentration in the soil, however, in the second year of experimentation Ca was added in rates equivalent to the plant available La content.

4.1 Influence of REEs on chemical soil characteristics

In general, a higher availability of REEs causes a higher REE uptake by plants. The availability of REEs in soils is closely related to the water soluble and exchangeable fractions of REEs and thus dependent on physico-chemical soil properties (Liang et al., 2000) such as pH, Eh, CEC, and clay content (Cao et al., 2001).

Among chemical soil properties, soil pH plays an important role in nutrient availability to plants. The effects of La, Ce, REE-fertilizer, Ca and Cu applications on soil pH and electrochemical conductivity are summarized in Table 4.1. The results shown in Table 4.1 reflect differences between treatments. The measurements of the soil electrochemical conductivity (EC) showed that REE applications (La, Ce, and REE-fertilizer) did not significantly influence this parameter in all treatments in 2005 (see Appendix Table B.1). In comparison, in 2006 soil EC values were significantly lower on non-vegetated soil when Ce was applied, but differences were only minor; on vegetated soil a significant reducing effect was found for Ce and La applications where maize was grown. In comparison, REE-fertilizer applications yielded a significant increase of EC values when maize was grown (Table 4.1).

Expectedly, the soil EC values for the Ca treatment increased highly significantly in 2005 because of the extra-ordinarily high amount of Ca that was applied here as a multiple of its plant available concentration (see Appendix, Table B.1). Soil EC values of vegetated and non-vegetated soil differed for all treatments. Compared with non-vegetated soil, vegetated soil had a lower salt content. The soil pH values were consistently higher on non-vegetated than vegetated soil in both years (Table 4.1 and see Appendix Table B.1).

Table 4.1: Influence of graded REE applications on some chemical soil characteristics of maize and oilseed rape 66 days after sowing (2005 and 2006) (averaged effects over all treatments)

Treatments	Soil pH			Soil EC (mS m^{-1})		
	Maize	Oilseed rape	Non-vegetated soil	Maize	Oilseed rape	Non-vegetated Soil
			2005			
Control	5.1 a	5.4 ab	6.2 c	130 a	154 a	402 ab
Lanthanum	5.3 ab	5.4 ab	6.1 abc	131 a	133 a	403 ab
Cerium	5.4 bc	5.4 a	6.0 ab	139 a	124 a	389 ab
REE-fertilizer	5.5 bc	5.5 ab	6.1 ab	150 a	153 a	396 ab
Calcium	5.6 a	5.6 b	6.2 ab	254 b	238 b	424 b
Copper	5.5 bc	5.6 ab	6.0 a	188 ab	192 ab	381 a
			2006			
Control	5.3 ab	5.2 a	6.0 a	46.7 ab	61.9 a	386 ab
Lanthanum	5.3 ab	5.2 a	6.1 ab	37.2 a	60.9 a	390 ab
Cerium	5.3 b	5.3 a	6.3 b	29.9 a	68.2 a	373 a
REE-fertilizer	5.1 a	5.2 a	6.1 ab	66.8 b	72.7 a	391 ab
Calcium	5.2 ab	5.2 a	6.2 ab	42.6 a	66.0 a	411 b

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

The results shown in Table 4.2 reflect differences for varying treatments in relation to dose. Graded rates of La had no influence on EC and soil pH when maize and oilseed rape were grown.

Table 4.2: Influence of graded REE applications on mean of soil pH (1:2.5) and soil electro-chemical conductivity (mS m^{-1}) of maize and oilseed rape 66 days after sowing (2006)

Application rate (µg g^{-1})	**Soil pH**			**Soil Electrochemical conductivity (mS m^{-1})**		
	Maize	**Oilseed rape**	**Non-vegetated soil**	**Maize**	**Oilseed rape**	**Non-vegetated soil**
Lanthanum						
0	5.3 a	5.2 a	6.0 a	46.7 a	61.9 a	386 a
1.0	5.2 a	5.2 a	6.2 b	38.9 a	55.2 a	431 b
10	5.2 a	5.2 a	6.0 a	37.8 a	60.4 a	390 ab
50	5.2 a	5.2 a	6.2 ab	40.6 a	57.8 a	372 a
100	5.4 a	5.3 a	6.0 a	31.8 a	70.4 a	366 a
Cerium						
0	5.3 a	5.2 a	6.0 a	46.7 b	61.9 a	386 ab
0.8	5.2 a	5.3 a	6.1 ab	29.5 a	65.7 a	360 ab
8.0	5.3 a	5.3 a	6.2 bc	30.7 ab	65.0 a	340 a
40	5.4 a	5.3 a	6.4 c	31.7 a	71.9 a	390 b
80	5.4 a	5.3 a	6.1 c	32.8 ab	70.1 a	401 b
REE-fertilizer						
0	5.3 a	5.2 ab	6.0 a	46.7 a	61.9 a	386 a
2.7	5.1 a	5.1 a	6.2 a	40.0 a	63.2 a	387 a
27	5.1 a	5.0 a	6.0 a	48.0 a	70.7 a	371 a
135	4.9 a	5.2 ab	6.2 a	66.5 a	61.7 a	401 a
270	5.1 a	5.4 b	5.9 a	112 b	95.1 b	418 a
Calcium						
0	5.3 a	5.2 ab	6.0 a	46.7 a	61.9 a	386 a
1.0	5.2 a	5.3 ab	6.1 ab	38.3 a	64.5 a	389 a
10	5.2 a	5.2 a	6.2 b	36.7 a	59.4 a	414 a
50	5.3 a	5.4 b	6.2 ab	42.0 a	67.6 a	405 a
100	5.2 a	5.1 a	6.2 ab	53.5 a	72.7 a	428 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

Graded rates of Ce reduced the EC values only when maize was grown; the influence of soil pH values proved to be not significant. Graded REE-fertilizer applications resulted in a steep increase of EC values, but only on the vegetated soil (Table 4.2). An RRE fertilizer rate of 270 µg g^{-1} and a Ca rate of 50 µg g^{-1} caused a significant increase of soil pH when oilseed rape was grown.

4.2 Influence of REEs on soil microbiological parameters

Soil is a complex environment, where microorganisms play a crucial role in nutrient cycling and degradation of pollutants (herbicides, pesticides, PAH-s, phenols, etc.), thus contributing to the maintenance of soil quality. On the other hand, microbial activities are strongly dependent on nutritional and other chemical and physical conditions of the soil and react rapidly to changes in soil properties. Microorganisms are considered sensible indicators when monitoring changes in soil status affected by agricultural management, but the meaningful set of microbiological indicators still remains an object of debate (Truu et al., 2008).

Soil microorganisms constitute a large dynamic source and sink of nutrients and play a major role in plant litter decomposition and nutrient cycling, soil structure, nitrogen fixation, mycorrhizal associations and reduction in plant pathogens (Kennedy and Smith, 1995). Moreover, they are very sensitive to environmental change, directly influence soil fertility levels, directly influence microbial viability, microbial biomass turnover, and microbial utilization efficiency of organic carbon (Liao and Xie, 2007)

The activity of soil microorganisms can be evaluated for instance by measuring respiration. Enzymes are biological catalysts of essential processes for the life of microorganisms and the simultaneous measurement of several enzyme activities may be useful for assessing soil microbial activity (Nannipieri et al., 1990). Among these activities are those related with the N (BAA-protease), P (phosphatase) and C (β-glucosidase) cycles (Bastida et al., 2008).

4.2.1 Influence of REEs on soil microbial counts

Soil microbes are a key component in soil ecosystems, dominating the cycling of nutrient elements and playing a major role in maintaining soil quality. Unfortunately, the soil microbial community is still a black box because of its complexity and the limitations of methodologies for quantification of the soil community. One gram of soil contains thousands of species and billions of individuals of microorganisms, but only approximately 2–3% of soil microbes have been described and less than 1% of the microbes are cultivable (Wang et al., 2008).

The effect of REE applications (Ce, La, and REE-fertilizer) on soil microbial counts (heterotrophic bacteria, actinomycetes and fungi) was tested in a pot experiment with maize and oilseed rape (Table 4.3). The number of heterotrophic bacteria was reduced by all treatments when compared to the control in 2006. The number of actinomycetes was reduced in the same year by the Ca treatment, but this effect was only significant when maize was grown. Ce had the strongest reducing effect on the number of fungi, while Cu increased this parameter significantly in 2005 when maize was grown. In case of oilseed rape differences between treatments were not significant in both years.

Table 4.3: Influence of graded REE applications on soil microbial counts of maize and oilseed rape 66 days after sowing (2005 and 2006) (averaged effects over all treatments)

Treatments	Maize			Oilseed rape		
	Heterotrophic bacteria	Actino-mycetes	Fungi	Heterotrophic bacteria	Actino-mycetes	Fungi
2005						
Control	6.6×10^5 a	1.8×10^6 a	1.1×10^5 ab	5.3×10^6 a	3.7×10^6 b	2.2×10^6 a
Lanthanum	3.9×10^7 a	2.3×10^6 a	1.0×10^5 ab	1.7×10^7 a	2.9×10^6 ab	2.2×10^6 a
Cerium	1.7×10^8 a	2.4×10^6 a	1.2×10^5 b	2.1×10^8 a	3.3×10^6 ab	1.3×10^6 a
REE-fertilizer	1.8×10^7 a	2.3×10^6 a	1.2×10^5 ab	2.0×10^7 a	3.1×10^6 ab	1.4×10^6 a
Calcium	6.3×10^7 a	1.6×10^6 a	5.5×10^5 ab	2.1×10^8 a	2.4×10^6ab	1.1×10^6 a
Copper	2.9×10^7 a	2.3×10^6 a	4.9×10^5 a	3.3×10^7 a	2.3×10^6 a	5.5×10^5 a
2006						
Control	5.5×10^6 a	9.6×10^5 a	2.9×10^6 bc	4.9×10^6 a	3.5×10^6 a	3.4×10^6 a
Lanthanum	3.4×10^7 b	1.8×10^6 ab	2.0×10^6 a	2.1×10^7 b	3.4×10^6 a	5.9×10^6 a
Cerium	3.4×10^7 b	1.6×10^6 ab	2.2×10^6 ab	3.6×10^6 a	1.9×10^6 a	6.2×10^6 a
REE-fertilizer	3.6×10^7 b	3.9×10^6 ab	3.2×10^6 c	3.6×10^6 a	2.9×10^6 a	5.2×10^6 a
Calcium	4.1×10^7 b	4.4×10^6 b	2.2×10^6 ab	3.8×10^6 a	2.9×10^6 a	6.1×10^6 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

The results presented in Tables 4.4 and B.2 (see Appendix) can be summarized as follows: counts of soil microorganisms (heterotrophic bacteria, actinomycetes and fungi) were generally not influenced by graded La, Ce, Ca and REE-fertilizer applications in 2005. La applications of 10 µg g^{-1} decreased the number of actinomycetes in soils grown with maize and oilseed rape. In contrast Ce had no significant effect on any of the measured parameters. Graded REE-fertilizer decreased significantly the number of fungi in pots grown with oilseed rape while this effect was not significant for maize. Interestingly, graded rates of Cu reduced all three microbial parameters irrespective of the crop.

In 2006, somewhat contrasting results were obtained. In general, graded La, Ce and REE-fertilizer applications resulted in a higher number of microbial counts, whereby this effect was more pronounced for maize. Also Ca rates equivalent to that of La and Ce yielded a significant increase in the number of heterotrophic bacteria and actinomycetes in maize pots (see Appendix Table B.2).

The relationships between soil pH, EC and microbiological parameters were tested for maize and oilseed rape and results are presented in Tables 4.5 and 4.6. The results presented in Tables 4.5 and 4.6 reveal that highly negative, significant correlation coefficients (r) were found between the number of fungi and soil EC and pH. The (r) values were -0.57**, -0.73** and -0.90, 0.37** for maize and oilseed rape, respectively (Figure 4.1). The same effect was observed for dehydrogenase activity (DHA) in the soil (Figure 4.4). Basic data for the influence of graded REE applications on soil enzymatic activities are presented in Table 4.7.

Table 4.4: Influence of graded REE applications on mean of soil microbial counts (CFU) of maize and oilseed rape 66 days after sowing (2005)

Application rate (µg g^{-1})	Maize			Oilseed rape		
	Heterotrophic bacteria	Actino-mycetes	Fungi	Heterotrophic bacteria	Actino-mycetes	Fungi
Lanthanum						
0	6.6×10^6 a	1.8×10^6 ab	1.1×10^6 a	5.3×10^6 a	3.7×10^6 b	1.9×10^6 a
1.0	3.5×10^7 ab	1.6×10^6 ab	1.1×10^6 a	5.1×10^6 a	1.8×10^6 a	1.6×10^6 a
10	1.8×10^7 a	1.1×10^6 a	5.6×10^5 a	5.1×10^7 b	3.0×10^6 ab	1.3×10^6 a
50	7.1×10^7 b	2.9×10^6 ab	1.3×10^6 a	4.9×10^6 a	3.3×10^6 b	1.2×10^6 a
100	3.3×10^7 ab	3.5×10^6 b	$1.1 x 10^6$ a	4.8×10^6 a	3.6×10^6 b	4.7×10^6 a
Cerium						
0	6.6×10^6 a	1.8×10^6 a	1.1×10^6 a	5.3×10^6 a	3.7×10^6 a	1.9×10^6 a
0.8	3.9×10^8 a	3.1×10^6 a	1.0×10^6 a	4.7×10^6 a	3.2×10^6 a	1.1×10^6 a
8.0	2.3×10^8 a	2.5×10^6 a	9.2×10^5 a	4.8×10^6 a	2.9×10^6 a	1.2×10^6 a
40	3.2×10^7 a	2.3×10^6 a	1.2×10^6 a	6.8×10^8 b	3.7×10^6 a	1.3×10^6 a
80	1.9×10^7 a	1.6×10^6 a	1.6×10^6 a	1.7×10^8 a	3.4×10^6 a	1.7×10^6 a
REE-fertilizer						
0	6.6×10^6 a	1.8×10^6 a	1.1×10^6 a	5.3×10^6 a	3.7×10^6 a	1.9×10^6 b
2.7	4.5×10^7 a	2.1×10^6 a	1.4×10^6 a	5.3×10^6 a	2.9×10^6 a	1.5×10^6 ab
27	1.7×10^7 a	2.2×10^6 a	1.0×10^6 a	2.8×10^7 b	3.5×10^6 a	1.7×10^6 ab
135	5.7×10^6 a	2.4×10^6 a	1.4×10^6 a	3.4×10^7 b	3.5×10^6 a	1.6×10^6 ab
270	5.3×10^6 a	2.7×10^6 a	8.2×10^5 a	1.1×10^7 a	2.6×10^6 a	6.9×10^5 a
Calcium						
0	6.6×10^6 a	1.8×10^6 a	1.1×10^6 a	5.3×10^6 a	3.7×10^6 b	1.9×10^6 a
9.83	1.6×10^7 a	6.7×10^6 a	1.2×10^6 b	5.9×10^7 a	2.6×10^6 ab	1.7×10^6 a
98.3	4.5×10^7 a	2.8×10^6 a	8.5×10^5 b	6.3×10^8 b	3.2×10^6 ab	2.8×10^6 a
491.5	1.6×10^6 a	1.6×10^6 a	1.3×10^5 a	3.7×10^7 a	1.8×10^6 a	2.1×10^5 a
983	1.9×10^8 a	1.4×10^6 a	3.7×10^4 a	1.2×10^8 a	1.9×10^6 ab	6.4×10^4 a
Copper						
0	6.6×10^6 c	1.8×10^6 ab	1.1×10^6 a	5.3×10^6 c	3.7×10^6 b	1.9×10^6 b
4.3	4.3×10^6 bc	2.5×10^6 ab	7.5×10^5 a	5.3×10^6 c	3.6×10^6 b	8.6×10^5 a
43	4.9×10^6 c	3.0×10^6 b	9.5×10^5 a	4.1×10^6 bc	2.9×10^6 b	3.9×10^5 a
215	4.6×10^5 a	2.6×10^6 ab	1.6×10^5 a	2.9×10^6 ab	2.4×10^6 b	2.6×10^5 a
430	2.1×10^6 ab	1.3×10^6 a	1.5×10^5 a	1.3×10^6 a	1.9×10^5 a	6.9×10^5 a

CFU, Colony Forming Unit g^{-1} dry soil
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

Table 4.5: Correlation coefficients (r) for the relation between soil pH and EC, AlP, DHA and microbial counts for **maize** 66 days after sowing (2005) (n=84)

	Soil pH	Soil EC	AlP	DHA	Microbial counts (CFU)		
					Heterotrophic bacteria	Actinomycetes	Fungi
Soil pH	-	.64**	.24*	- .39**	.13	- .07	- .57**
Soil EC		-	.08	- .58**	.04	- .24*	- .73**
AlP			-	.43**	.21	.11	- .04
DHA				-	.14	.18	.65**
Bacteria					-	.28**	- .01
Actinomycetes						-	.22*
Fungi							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed).
Soil EC, Soil electrical conductivity (mS m^{-1}), AlP, alkaline phosphatase activity, DHA, dehydrogenase activity

Table 4.6: Correlation coefficients (r) for the relation between soil pH and EC, AlP, DHA and microbial counts for **oilseed rape** 66 days after sowing (2005)

	Soil pH	**Soil EC**	**AlP**	**DHA**	**Microbial counts (CFU)**		
					Heterotrophic bacteria	**Actinomycetes**	**Fungi**
Soil pH	-	.30**	.05	.05	.04	.18	- .09
Soil EC		-	- .05	- .61**	- .09	- .41**	- .37**
AlP			-	.06	- .04	.09	.02
DHA				-	.18	.18	.11
Bacteria					-	.56**	.23**
Actinomycetes						-	.36**
Fungi							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed).
Soil EC, Soil electrical conductivity (mS m^{-1}), AlP, alkaline phosphatase activity, DHA, dehydrogenase activity

In 2005, graded REE applications significantly influenced the number of actinomycetes; a promoting influence was determined for maize and a decreasing effect for oilseed rape (Table 4.4). It was observed also that all soil microbial counts decreased by increasing Cu and Ca applications for maize and oilseed rape in 2005. Figure 4.1 shows the relationship between soil EC and fungal counts in soils when maize was grown, which was negative (r= - 0.73**). The results suggest that growth conditions for fungi are worsening when the salt content in the soil increases.

Figure 4.2 shows the different tolerance of the soil microbial community to graded Cu application rates when maize and oilseed rape were grown. In general, the microbial counts decreased in the order heterotrophic bacteria > actinomycetes > fungi. The soil microbial community was significantly affected by Cu additions in presence of oilseed rape. In case of maize the number of fungi was reduced, however not significantly. Soil microbial communities decreased by increasing of Cu application rates for both crops. Only the number of actinomycetes increased significantly up to a Cu rate of 43 µg g^{-1} when maize was grown in 2005 (Table 4.4).

In 2006, heterotrophic bacteria and actinomycetes were significantly influenced by all treatments in case of maize, whereas only heterotrophic bacteria had this behavior in case of oilseed rape as shown in Table B.2 (see Appendix). It was observed that the number of heterotrophic bacteria and actinomycetes significantly increased in case of maize for all treatments as following: for La, Ce, REE-fertilizer and Ca the microbial number increased up to levels of (50, 50), (40, 40), (2.7, 27), and (50, 50) for heterotrophic bacteria and actinomycetes, respectively.

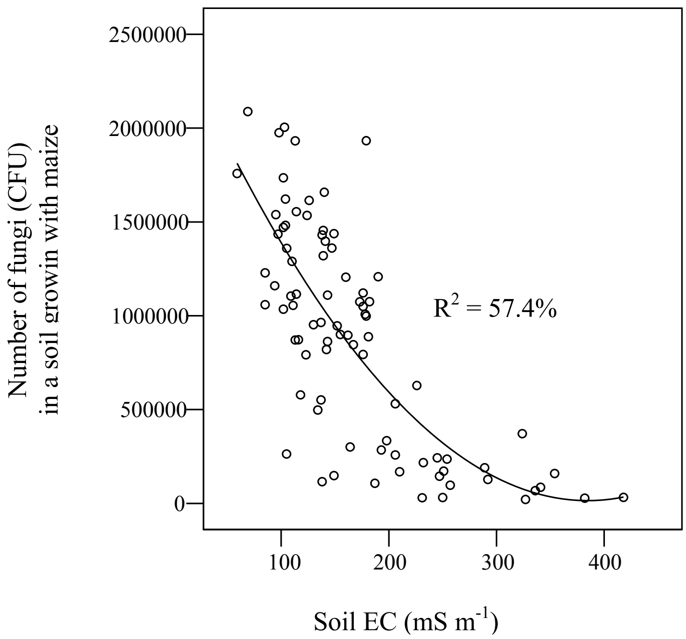


Figure 4.1: Relation between soil EC and number of fungi in a soil grown with maize 66 days after sowing (2005)

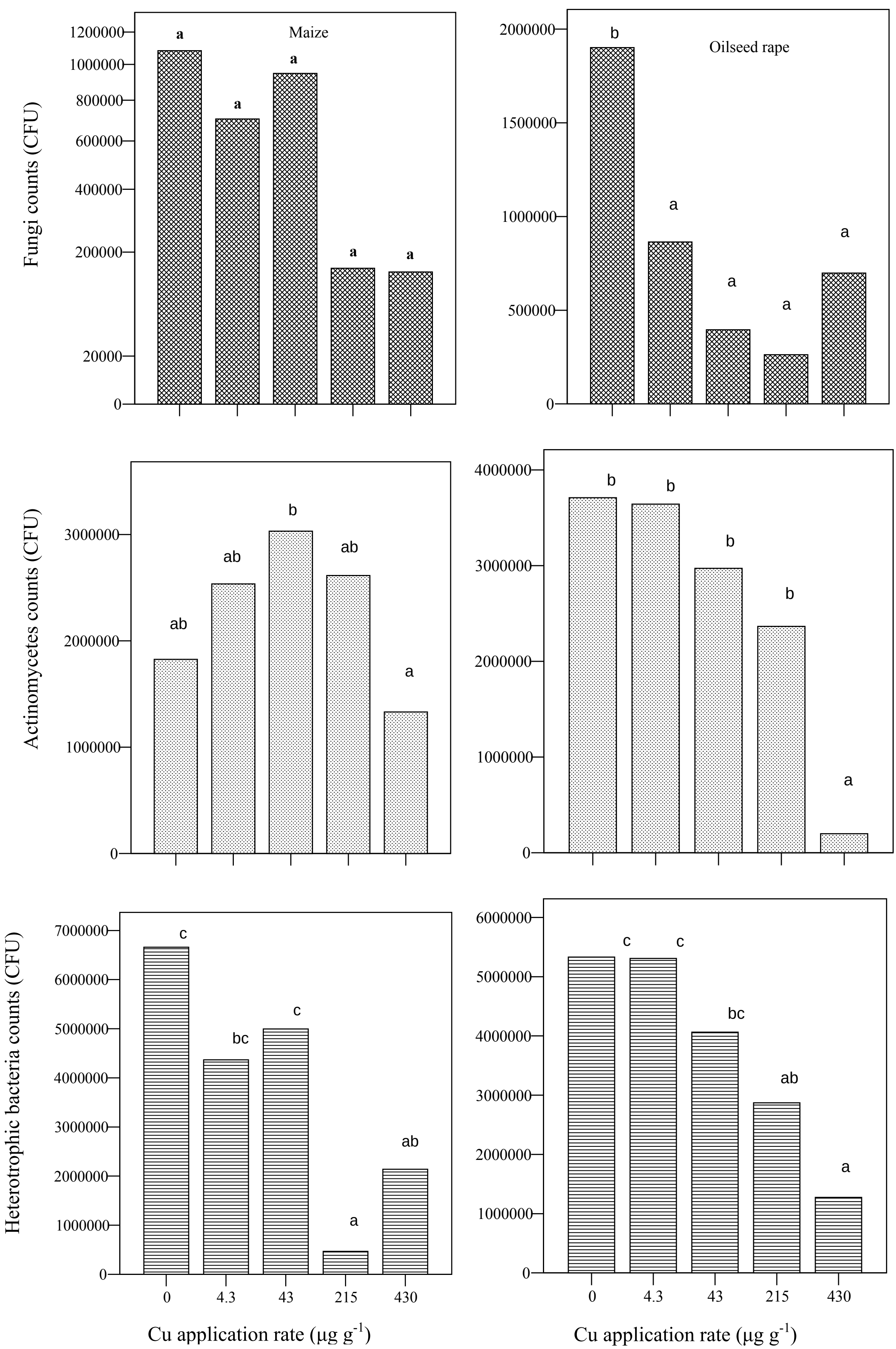


Figure 4.2: Comparison of the effect of graded Cu applications on microbial counts (heterotrophic bacteria, fungi and actinomycetes) for maize and oilseed rape 66 days after sowing (2005)

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

4.2.2 Influence of REEs on soil enzyme activities

Soil is a living dynamic system containing many free enzymes, immobilized extra-cellular enzymes and enzymes within microbial cells (Skujins, 1978). Enzymes present in soil are similar to enzymes in other systems. Their reaction rates are closely related to pH, ionic strength, temperature, and the presence or absence of inhibitors (Tabatabai, 1982). The soil enzymes include a wide spectrum of oxide-reductase, transferases, hydrolases and lysases. The enzymes mostly found in soil are dehydrogenases, catalase, phosphatase, amylase, cellulase, pectinase, saccharase, protease, urease, arginine deaminase, nitrate reductase etc. These are generally of bacterial or fungal origin and only a small fraction is excreted by animals or plants. They act intra or extra-cellular and are responsible for most of the biochemical reaction in soil. The role of soil enzymes is important in terms of ecosystem functioning (Burns, 1982). The most valuable use of soil enzymes is to assess the effects of various anthropogenic activities and chemicals on soil life. Numerous studies have been conducted to determine the changes in soil enzyme activities caused by acid rain, heavy metals, fertilizers, pesticides, industrial and other agricultural chemicals. Soil enzymes are indicators of microbial activities in soil and are often considered as an indicator of soil health and fertility. They are very sensitive to agricultural practices, soil pH, nutrients, inhibitors and weather conditions (Singh and Kumar, 2008).

In this study, dehydrogenase (DHA) and alkaline phosphatase (AlP) activities were measured. As mentioned before, dehydrogenase activity is considered as a suitable indicator of microbial activity because dehydrogenase only occurs within living cells (it is an intracellular process that occurs in every viable microbial cell and is measured to determine overall microbiological activity of soil). Alkaline phosphatase (AlP) is responsible for organic P transformations in the soil. AlP originates from extracellular and intracellular enzyme activities (Eichler et al., 2004). The only source of AlP in soils is micro-organisms.

Influence of REEs on dehydrogenase activity and alkaline phosphatase activity

The influence of graded REE applications on soil enzymes activities (DHA and AlP) was determined and results are presented in Table 4.7. In general, REE applications (La, Ce, and REE-fertilizer) decreased DHA and AlP activities (see Appendix Table B.3). The lowest DHA activities were found on the non-vegetated soil. The AlP activity was regularly higher on the non-vegetated soil in 2005 (Table 4.7)

Table 4.7: Influence of graded REE applications on some soil enzyme activities of maize and oilseed rape 66 days after sowing (2005 and 2006) (averaged effects over all treatments)

Treatments	Dehydrogenase activity (TPF)			Alkaline phosphatase activity (p-NP)		
	Maize	Oilseed rape	Non-vegetated soil	Maize	Oilseed rape	Non-vegetated Soil
			2005			
Control	16.6 bc	19.5 b	3.1 ab	72.2a	133 a	185 b
Lanthanum	17.6 c	19.9 b	3.5 b	107 a	90.4 a	200 b
Cerium	15.2 bc	20.6 b	3.2 ab	95.4 a	108 a	172 b
REE-fertilizer	14.2 bc	19.8 b	3.1 ab	63.0 a	102 a	144 ab
Calcium	12.6 b	17.6 b	3.4 ab	103 a	100 a	145 ab
Copper	7.2 a	7.4 a	1.9 a	60.1a	110 a	86.4 a
			2006			
Control	26.0 a	26.9 b	0.93 a	181 a	140 a	26.6 a
Lanthanum	26.6 a	26.0 b	1.11 a	185 a	126 a	145 a
Cerium	26.8 a	24.5 ab	0.86 a	797 b	134 a	132 a
REE-fertilizer	21.6 a	21.3 a	0.69 a	110 a	170 a	121 a
Calcium	27.1 a	22.9 a	0.82 a	145 a	149 a	137 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

The results shown in Table 4.7 reflect differences between treatments. Differences for La, Ce, Ca and REE-fertilizer proved to be significant only in 2005 on non-vegetated soil when the AlP activity was highest in the control, La and Ce treatment and in 2006 when the DHA activity was significantly lower when REE-fertilizer was applied and oilseed rape grown.

Results show that there was no significant effect of graded REE-fertilizer applications on AlP in the non-vegetated soil in both seasons, whereas Cu, La and Ce applications affected significantly the AlP activity (Table 4.8). Ce application rates significantly affected AlP when maize and oilseed rape was grown in 2006. La and Ca application rates did not significantly affect AlP activity in vegetated soils (Table 4.8). Graded Cu applications yielded on vegetated and non-vegetated soil consistently a significant reduction of the AlP and DHA in 2005 (Table 4.8).

In case of DHA, non-significant effects of graded REE applications (La, Ce, and REE-fertilizer) were observed in the non-vegetated soil. In contrast, graded REE applications (except La) affected significantly DHA activities when oilseed rape was grown in 2006. In case of maize, graded applications of La and Ce yielded effects that were not significant, while that of graded REE-fertilizer applications proved to significantly decrease both enzyme activities on the vegetated soils in both seasons (Table 4.8). The lowest DHA activities were found in the non-vegetated soil in both seasons.

Results presented in Tables 4.9a, b and 4.10a, b show the correlation coefficients for the relationships between soil pH and EC and enzyme activities (DHA and AlP) in vegetated and non-vegetated soils. Negative correlation coefficients (r) were determined (r= – 0.27*, r=

– 0.07) for oilseed rape and (r= – 0.31**, r= – 0.29**) and maize in 2005 and 2006 for AlP, respectively) between soil pH and EC, and soil enzymes. Relationships (r= – 0.13 and r= – 0.19) between DHA and soil EC were not significant for maize and oilseed rape, respectively. According to the results shown in Tables 4.9 and 4.10, the closest relationships existed between soil EC and DHA activity (Figure 4.3). These Tables do not reflect the role chemical soil properties and soil enzyme activities only in the presence and absent of plants but also plant species have a particular impact on these previous characteristics. This means, plants root exudates for example have different effects on soil biological activities.

Table 4.8: Influence of graded REE applications on mean of soil enzyme activities of maize and oilseed rape 66 days after sowing (2006)

Application rate ($\mu g\ g^{-1}$)	Dehydrogenase activity (TPF)			Alkaline phosphatase activity (p-NP)		
	Maize	**Oilseed rape**	**Non-vegetated soil**	**Maize**	**Oilseed rape**	**Non-vegetated soil**
Lanthanum						
0	26.0 a	26.9 a	1.7 a	181 a	140 a	126 a
1.0	24.2 a	28.6 a	1.2 a	181 a	110 a	106 a
10	25.1 a	24.4 a	0.9 a	181 a	132 a	205 b
50	28.6 a	26.9 a	1.0 a	162 a	132 a	144 a
100	28.0 a	27.6 a	1.2 a	215 a	130 a	125 a
Cerium						
0	26.0 a	26.9 b	1.7 a	181 a	140 ab	126 a
0.8	27.1 a	21.0 a	1.0 a	1202 c	106 a	159 a
8.0	25.9 a	23.0 ab	0.8 a	1075 c	115 a	114 a
40	28.7 a	27.3 b	0.9 a	793 b	147 ab	116 a
80	25.1 a	26.7 b	0.7 a	117 a	167 b	139 a
REE-fertilizer						
0	26.0 b	26.9 b	1.7 b	181 b	140 a	126 a
2.7	25.3 b	20.2 a	0.6 ab	126 ab	201 a	136 a
27	23.7 ab	20.1 a	1.1 ab	84.9 a	160 a	112 a
135	21.6 ab	21.8 ab	0.4 a	83.5 a	136 a	111 a
270	16.7 a	23.0 ab	0.9 ab	146 ab	183 a	124 a
Calcium						
0	26.0 a	26.9 b	1.7 b	181 a	140 a	126 a
1.0	25.5 a	24.5 ab	1.6 b	149 a	128 a	136 a
10	28.9 a	22.3 ab	0.9 ab	160 a	134 a	94.6 a
50	27.4 a	25.3 b	0.3 a	152 a	165 a	156 a
100	26.5 a	19.6 a	0.4 ab	121 a	168 a	164 a

p-NP, µg p-nitrophenol $.g^{-1}\ .dm^{-1}.\ h^{-1}$
TPF, Triphenylformazan [$\mu g\ g^{-1}$ DM d^{-1}]
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

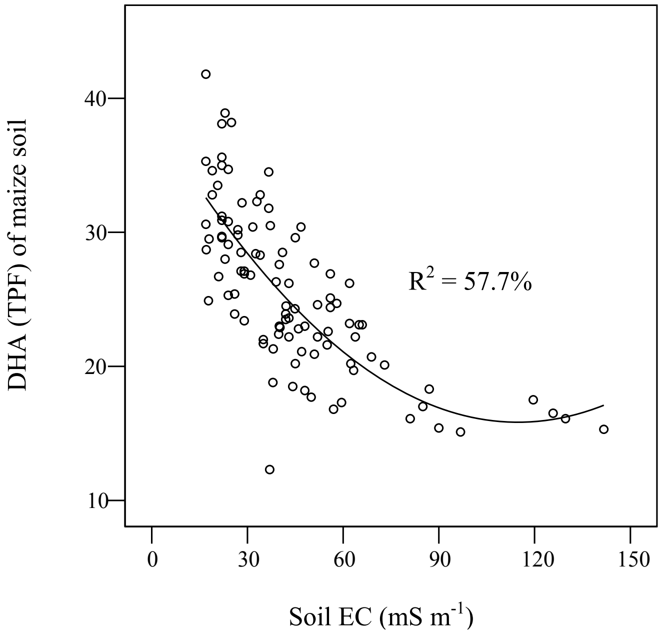


Figure 4.3: Relation between soil EC and DHA on a soil grown with maize 66 days after sowing (2005) (n= 84)

Table 4.9a: Correlation coefficients (r) for the relation between soil pH and EC, AlP and DHA on soils grown with **oilseed rape** and **non-vegetated soil** 66 days after sowing (2005)

		Non-vegetated soil (n=84)			
		Soil pH	**Soil EC**	**AlP**	**DHA**
Oilseed rape	**Soil pH**	.27**	.27*	- .07	.20
(n=84)	**Soil EC**		.54**	- .27*	- .10
	AlP			.35**	.003
	DHA				.54**

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Table 4.9b: Correlation coefficients (r) for the relation between soil pH and EC, AlP and DHA on soils grown with **maize** and **non-vegetated soil** 66 days after sowing (2005)

		Non-vegetated soil (n=84)			
		Soil pH	**Soil EC**	**AlP**	**DHA**
Maize	**Soil pH**	.09	- .20	- .49	.01
(n=84)	**Soil EC**		.28*	.01	.001
	AlP			.01	.05
	DHA				- .11

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed).

Table 4.10a: Correlation coefficients (r) for the relation between soil pH and EC, AlP and DHA on soils grown with **oilseed rape** and **non-vegetated soil** 66 days after sowing (2006)

		Non-vegetated soil (n=84)			
		Soil pH	**Soil EC**	**AlP**	**DHA**
Oilseed rape	**Soil pH**	- .003	- .09	- .03	.04
(n=102)	**Soil EC**		.16	- .04	- .19
	AlP			- .05	- .36**
	DHA				.23

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Table 4.10b: Correlation coefficients (r) for the relation between soil pH and EC, AlP and DHA on soils grown with **maize** and **non-vegetated soil** 66 days after sowing (2006)

		Non-vegetated soil (n=84)			
		Soil EC	**AlP**	**DHA**	**Soil pH**
Maize	**Soil pH**	- .03	.47**	- .31**	.02
(n=102)	**Soil EC**		.41**	- .29**	- .13
	AlP			.27*	.49**
	DHA				.56**

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

4.3 Influence of REEs on plant features

The soil-plant transfer of elements is part of their cycling in nature. Total concentration of chemical elements in soils can not be considered as a good indicator of their bioavailability (Wang et al., 2004). The evaluation of bioavailable trace elements is of crucial importance since it allows the assessment of the plant's potential to mobilize or to accumulate metals from the soil (Branquinho et al., 2007). In return uptake of essential and other mineral elements affects plant metabolism and is consequently expressed by differences in mineral composition and crop growth parameters.

The concentration of REEs remarkably increased in soil ecosystems and has become a serious environmental problem (Zhimang et al., 2001). In the last 20 years, many researchers reported on transportation, transformation, content and distribution of REEs in soil and plant systems (Guo, 1999). Recently, the effects of organic ligands on the bioaccumulation and bioavailability of REEs in the soil-plant ecosystem (Yang et al., 1999) and in aqueous system (Tu et al., 1994) have been investigated, but less work has been done on the effects of organic matter in soil ecosystems. In natural soil system, organic ligands, such as organic acid, fulvic acid (FA), humic acid, plant root exudates, etc., play an important role in altering the bioavailability of REEs in soil by complexion (Zhimang et al., 2001).

Redistribution of an element from old to young plant organs mainly takes place via the phloem (Marschner, 1995). The redistribution of REEs in wheat showed that REE contents were extremely low in the young leaves. This indicates a restricted phloem transport of REEs. The acropetal transport via the xylem obviously plays a key role for the accumulation of REEs (Ding et al., 2005).

In the following sections the influence of graded La, Ce and REE-fertilizer applications on yield parameters of maize and oilseed rape, and uptake of mineral elements and REEs will be shown.

4.3.1 Influence of REEs on yield parameters

The results from the few existing studies on the effect of REEs on plant growth are contradictory. Early reports indicated that REEs were inhibitory on plant growth. As mentioned before, although there is no clear evidence that REEs are essential minerals for plant growth, many studies suggested that REEs stimulate plants to take up, translocate and assimilate nutrients (Pang et al., 2002). REEs have been used in agriculture since the early last century, but only recently a few reviews of REE effects on crop performance have become available internationally (see chapter 1).

Pot experiments were carried out using graded doses of REE-fertilizer, La, Ce (as an important component of this fertilizer), Ca (to compare with La and other REEs) and Cu (to evaluate and compare at the same time with possibly toxic effect of REEs) for studying their influence on yield parameters of maize and oilseed rape.

Table 4.11 shows the influence of graded REE applications (La, Ce, REE-fertilizer) and Ca on germination rate and plant height of maize and oilseed rape. The results clearly reveal that only the application of the highest dose of REE-fertilizer (270 $\mu g\ g^{-1}$) yielded a significant decrease of the germination rate of maize, while the reduction oilseed rape was not significant (for more details see Appendix Table B.5). In 2005, all plants died off when the third and fourth-fold plant available content of Ca and Cu was applied due to salt and heavy metal stress.

Effects of La, Ce, Ca, Cu and REE-fertilizer on plant biomass proved to be statistically not significant in case of maize in 2005 (Table 4.12). In comparison, in 2006 all treatments had a significant effect on roots and shoot biomass of maize. In case of oilseed rape, there was a diverse behavior in such way that in 2005 total biomass production was significantly reduced, while differences were not significant in 2006 (Figure 4.4). In Figure 4.4 and Tables 4.13 and B.4 (in Appendix), it could be observed that graded REE-fertilizer application rates increased the total biomass production up to levels of 2.7 and 2.7 $\mu g\ g^{-1}$ for maize and 27 and 2.7 $\mu g\ g^{-1}$ for oilseed rape in 2005 and 2006, respectively.

Table 4.11: Influence of graded REE applications on mean values for germination rate and plant height of maize and oilseed rape 66 days after sowing (2006)

Application rate (µg g^{-1})	Maize		Oilseed rape	
	Germination rate (%)	Plant height (cm)	Germination rate (%)	Plant height (cm)
Lanthanum				
0	100 a	73.3 a	95.8 a	29.7 a
1.0	100 a	79.8 a	95.8 a	28.9 a
10	100 a	80.0 a	100 a	29.7 a
50	100 a	87.4 a	95.8 a	28.9 a
100	83.3 a	77.0 a	95.8 a	27.4 a
Cerium				
0	100 a	73.3 a	95.8 a	29.7 a
0.8	100 a	81.2 a	95.8 a	31.7 a
8.0	100 a	82.0 a	100 a	31.9 a
40	100 a	83.1 a	100 a	31.0 a
80	100 a	79.5 a	100 a	29.2 a
REE-fertilizer				
0	100 b	73.3 b	95.8 a	29.7 bc
2.7	100 b	77.7 b	95.8 a	33.5 c
27	100 b	78.1 b	95.8 a	24.7 ab
135	100 b	72.0 b	100 a	26.7 abc
270	83.8 a	52.3 a	100 a	22.1 a
Calcium				
0	100 a	73.3 a	95.8 a	29.7 a
1.0	100 a	78.1 a	100 a	29.6 a
10	100 a	76.8 a	100 a	31.0 a
50	100 a	78.7 a	100 a	34.6 a
100	94.4 a	72.7 a	100 a	31.2 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

Table 4.12: Influence of graded REE applications on plant biomass production of maize and oilseed rape 66 days after sowing (2005 and 2006) (averaged effects over all treatments)

Treatments	Maize			Oilseed rape		
	Roots	Shoots	Total biomass	Roots	Shoots	Total biomass
			2005			
Control	3.9 a	11.6 a	15.5 a	1.0 a	9.0 ab	10.0 ab
Lanthanum	2.9 a	10.8 a	13.7 a	1.8 a	15.4 ab	17.2 ab
Cerium	3.1 a	10.7 a	13.8 a	1.9 a	20.3 b	22.2 b
REE-fertilizer	3.8 a	10.4 a	14.2 a	1.9 a	15.1 ab	17.1 ab
Calcium	3.1 a	8.0 a	11.1 a	1.5 a	11.7 ab	13.2 ab
Copper	4.7 a	12.8 a	17.5 a	0.8 a	6.6 a	6.4 a
			2006			
Control	10.1 ab	16.5 a	26.3 a	4.5 a	9.0 a	13.7 a
Lanthanum	9.7 ab	20.2 ab	30.4 a	4.1 a	8.9 a	13.2 a
Cerium	11.6 b	24.2 b	36.1 a	3.9 a	9.2 a	12.9 a
REE-fertilizer	7.7 a	18.4 ab	26.1 a	3.7 a	9.6 a	13.2 a
Calcium	10.2 b	22.7 ab	32.8 a	4.3 a	9.8 a	14.1 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

Table 4.13 shows that there was not any statistically significant effect for different rates of REEs on plant biomass when oilseed rape was grown in 2006. In case of maize, only REE-fertilizer application rates significantly reduced plant biomass production. The same trend was observed for maize and oilseed rape in 2005 (see Appendix Table B.4).

Table 4.13: Influence of graded REE applications on mean of biomass production (g pot^{-1}) of maize and oilseed rape 66 days after sowing (2006)

Application rate	Maize biomass production (g pot^{-1})			Oilseed rape biomass production (g pot^{-1})		
(µg g^{-1})	Roots	Shoots	Total	Roots	Shoots	Total
Lanthanum						
0	10.0 a	-----*	----*	4.5 a	9.0 a	13.5 a
1.0	9.6 a	-----*	----*	4.2 a	9.2 a	13.5 a
10	8.9 a	-----*	----*	3.9 a	8.7 a	12.9 a
50	9.0 a	-----*	----*	3.8 a	8.4 a	12.6 a
100	11.6 a	-----*	----*	4.4 a	8.8 a	13.5 a
Cerium						
0	10.0 a	16.5 a	26.4 a	4.5 a	9.0 a	13.5 a
0.8	11.3 a	23.8 b	35.4 b	3.7 a	8.7 a	12.1 a
8.0	11.0 a	24.8 b	36.2 b	4.1 a	9.8 a	14.0 a
40	11.8 a	24.6 b	36.8 b	3.8 a	9.6 a	12.8 a
80	12.0 a	23.5 b	35.6 b	3.6 a	9.0 a	12.7 a
REE-fertilizer						
0	10.0 b	16.5 ab	26.4 b	4.5 a	9.0 a	13.5 a
2.7	10.1 b	21.3 b	31.5 b	4.0 a	9.8 a	13.8 a
27	8.8 b	22.2 b	31.0 b	3.7 a	9.8 a	13.5 a
135	7.8 b	2.1 b	28.0 b	3.9 a	9.1 a	13.0 a
270	4.0 a	10.0 a	14.0 a	3.1 a	9.4 a	12.5 a
Calcium						
0	10.0 a	16.5 a	26.4 a	4.5 a	9.0 a	13.5 a
1.0	10.8 a	23.6 a	34.5 a	4.7 a	9.6 a	14.3 a
10	10.3 a	23.1 a	33.8 a	4.4 a	9.8 a	14.3 a
50	10.2 a	22.7 a	33.3 a	4.5 a	9.7 a	14.4 a
100	9.3 a	19.7 a	29.2 a	3.5 a	9.9 a	13.5 a

* No data. Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

In Tables 4.14-4.17 the relationships between root, shoot and total biomass production and germination rate and plant height were determined. In 2006, when maize was grown germination rate correlated significantly with plant height and plant biomass (root dry matter, shoot dry matter and total biomass). The correlation coefficients (r) were r=0.06, r=0.82** and r=0.84** for the relationship between plant height and root, shoot and total biomass of maize in 2006 (Table 4.16). For the corresponding relationship between germination rate and root, shoot and total biomass (Table 4.16) the correlation coefficients were (r=0.41**, r=0.49** and r=0.49**).

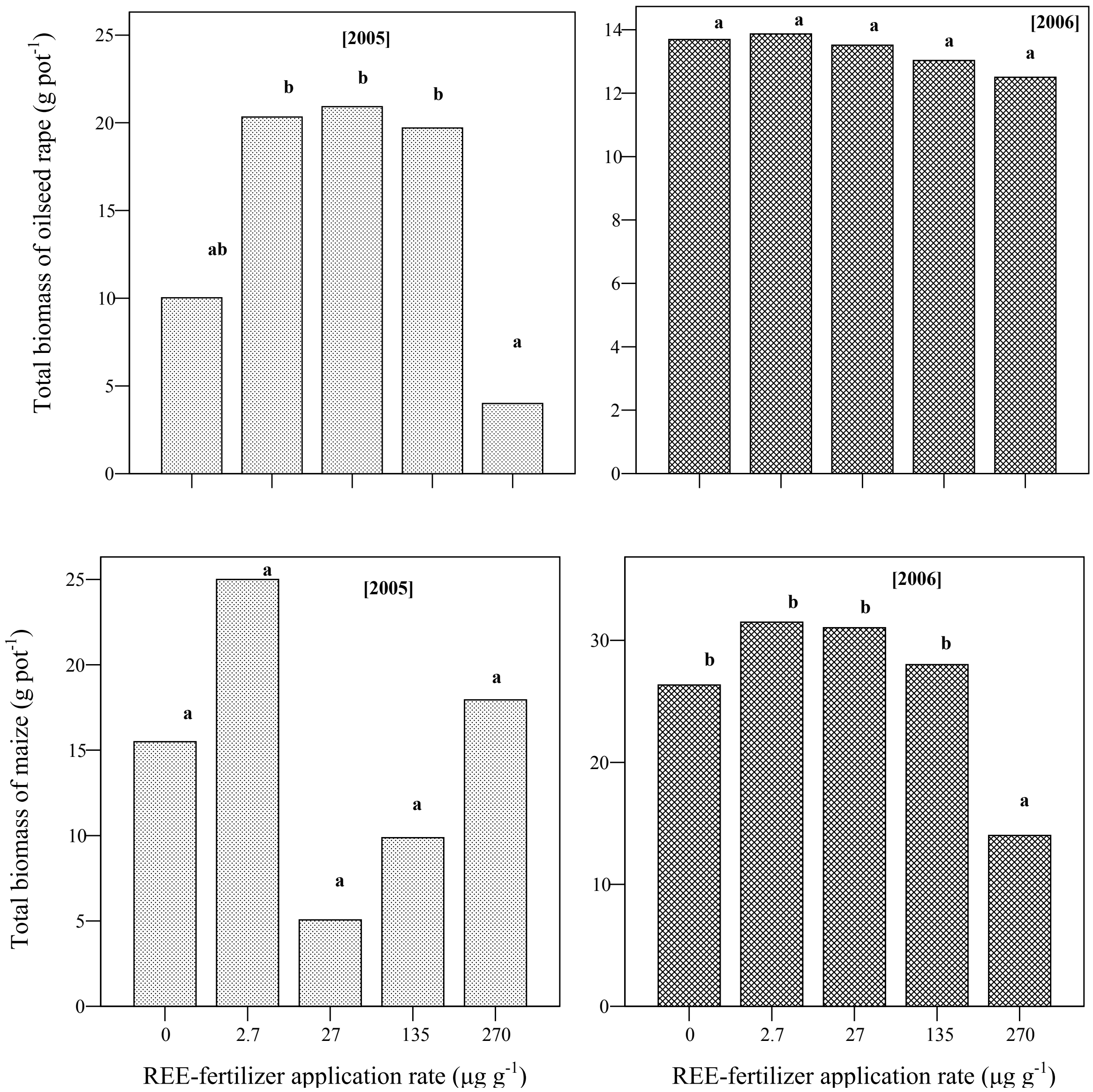


Figure 4.4: Effect of graded REE-fertilizer application rates on maize and oilseed rape biomass production (2005 and 2006). Values followed by the same letters are not significantly different by Tukey's test at 0.05 levels

Table 4.14: Correlation coefficients (r) for the relation between biomass production, germination rate and plant height for **maize** 66 days after sowing (2005) (n= 84)

	Biomass production			Germination rate	Plant height
	Roots	**Shoots**	**Total biomass**		
Roots	-	.93**	.96**	.19	.36**
Shoots		-	.99**	.19	.45**
Total biomass			-	.19	.44**
Germination rate				-	.14
Plant height					-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Table 4.15: Correlation coefficients (r) for the relation between biomass production, germination rate and plant height for **oilseed rape** 66 days after sowing (2005) (n= 84)

	Biomass production			Germination rate	Plant height
	Roots	Shoots	Total biomass		
Roots	-	.64**	.71**	.55**	.28*
Shoots		-	.99**	.45**	.33**
Total biomass			-	.48**	.33**
Germination rate				-	.29*
Plant height					-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Striking is the fact that there was no significant correlation between germination rate and any plant growth parameter when maize was cultivated, while for oilseed rape this feature was positively and significantly correlated with biomass production in 2005 (Table 4.14 and 4.15). In 2006, inverse results were determined for both crops (Table 4.16 and 4.17). In the second year of experimentation plant height of oilseed rape showed also no relationship with any other parameter.

Table 4.16: Correlation coefficients (r) for the relation between biomass production, germination rate and plant height for **maize** 66 days after sowing (2006) (n= 102)

	Biomass production			Germination rate	Plant height
	Roots	Shoots	Total biomass		
Roots	-	.85**	.94**	.41**	.06
Shoots		-	.98**	.49**	.82**
Total biomass			-	.49**	.84**
Germination rate				-	.09
Plant height					-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Table 4.17: Correlation coefficients (r) for the relationship between biomass production, germination rate and plant height for **oilseed rape** 66 days after sowing (2006) (n= 102)

	Biomass production			Germination rate	Plant height
	Roots	Shoots	Total biomass		
Roots	-	.22*	.72**	.02	.17
Shoots		-	.84**	.18	.14
Total biomass			-	.13	.19
Germination rate				-	.06
Plant height					-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

In Figures 4.5 to 4.7, the influence of graded REE-fertilizer and La applications on growth of maize and oilseed rape is visualized by photographs (for more photos see Appendix).

Control 2.7 27 135 270 Control 2.7 27 135 270

REE-fertilizer rates (µg g^{-1})

Figure 4.5: Influence of graded REE-fertilizer applications on biomass production of maize (2006) (see Appendix)

Control 2.7 27 135 270 Control 2.7 27 135 270

REE-fertilizer application rates (µg g^{-1})

Figure 4.6: Influence of graded REE-fertilizer application rates on biomass production of oilseed rape (2006)

Control 1.0 10 50 100 Control 1.0 10 50 100

La application rates (µg g^{-1})

Figure 4.7: Influence of graded La applications on biomass production of maize (2006)

4.3.2 Influence of REE applications on the concentration of macro and micro-nutrients in oilseed rape and maize

Essential nutrients and beneficial elements often unfold symptoms of toxicity in plants when supplied at excessive concentrations. The identification of threshold concentrations for the toxicity of La and Ce to plants is essential for setting up response curves of an increasing supply with both elements. Change in root length provides a rapid and sensitive indicator of toxicity. Other parameters are for instance yield components and macroscopic symptoms of toxicity.

From previous information, it can be concluded that REE applications yield beneficial, inhibitory and toxic effects. In addition, it was shown that toxic REE concentrations vary between crop species. Generally, except for oilseed rape, an increase of growth was expected by the application of less than 1 g kg^{-1} rare earth oxides to the soil, while the use of more than 1-2 g kg^{-1} rare earth oxides caused inhibitory effects (Chang et al., 1998). Zhang and Taylor (1988) attributed the response to REE application to a combination of factors. These factors include soil properties such as pH, organic matter and mineral content, methods, rates and timing of REE applications, crop conditions such as variety and growth stage, as well as weather conditions (Redling, 2006).

Concentration and uptake of REEs

Plants were divided into two parts (roots and shoots) at sampling 35 and 66 days after sowing in order to measure the concentration of individual REEs and selected essential macro and micro nutrients in these plant organs and to calculate the uptake of REEs in different tissues. Tables 4.18a and b show the concentration and uptake of REEs in roots and shoots of maize and oilseed rape in 2006 (for other data of 2005 see Appendix Tables B.6- B.15). The results shown in Tables 4.18a and b reveal that the REE content of roots and shoots increased with increasing REE application (La, Ce and REE-fertilizer). The highest concentration of REEs was found in roots when compared to shoots of oilseed rape and maize. It was found that accumulation of REEs in different parts of plants decreased in the following order: root > shoots and REEs in the order: Ce > La > Nd >Pr for each plant part and for each crop.

Table 4.18a: Influence of graded REE-fertilizer application rates on mean REE concentration (µg g^{-1}) in roots and shoots of maize and oilseed rape 66 days after sowing (2006)

REE-fertilizer application rates (µg g^{-1})	Roots of maize				Shoots of maize			
	La	Ce	Pr	Nd	La	Ce	Pr	Nd
0	4.24 a	8.84 a	0.89 a	3.28 a	0.09 a	0.23 a	<0.05	<0.05
2.7	4.73 a	9.83 a	1.02 a	3.64 a	0.06 a	0.09 a	<0.05	0.07
27	10.1 a	19.7 a	2.01 a	6.82 a	0.15 a	0.24 a	<0.05	0.08
135	33.9 a	58.1 a	5.84 a	18.9 a	0.43 a	0.51 a	0.07	0.16
270	120 b	180 b	17.9 b	56.7 b	1.68 b	1.79 b	0.18	0.58
	Roots of oilseed rape				Shoots of oilseed rape			
0	9.54 a	19.14 a	1.89 a	6.78 a	0.23 a	0.38 a	<0.05	0.13 a
2.7	11.2 a	20.9 a	2.10 a	7.35 a	0.23 a	0.36 a	0.07	0.12 a
27	29.9 a	50.5 a	5.06 a	16.4 a	0.79 a	1.13 a	0.12	0.35 a
135	104 b	161 b	15.7 b	48.6 b	2.47 b	3.75 b	0.41	1.36 b
270	163 c	235 c	21.9 c	67.2 c	3.74 c	5.66 c	0.61	2.01 c

*< lower limit of quantitation
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

Table 4.18b: Influence of graded REE-fertilizer application rates on mean of REE uptake (µg pot^{-1}) by maize and oilseed rape 66 days after sowing (2006)

REE-fertilizer application rates (µg g^{-1})	Uptake by maize roots (µg pot^{-1})				Uptake by maize shoots (µg pot^{-1})			
	La	Ce	Pr	Nd	La	Ce	Pr	Nd
0	43.2 a	89.9 a	9.1 a	33.4 a	1.6 ab	3.8 ab	----*	1.0
2.7	48.2 ab	100 ab	10.4 ab	37.2 ab	1.3 a	1.8 a	-----*	1.4
27	89.4 b	174 b	17.7 b	60.3 b	3.4 a	5.3 ab	-----*	1.7
135	252 c	432 c	43.5 c	141 c	8.1 b	9.6 b	0.5	3.1
270	406 d	617 d	61.2 d	194 d	14.7 c	16.2 c	1.6	5.2
	Uptake by oilseed rape roots (µg pot^{-1})				Uptake by oilseed rape shoots (µg pot^{-1})			
0	43.3 a	86.3 a	8.6 a	30.7 a	2.1 a	3.6 a	1.1	1.2 a
2.7	46.6 a	86.9 a	8.7 a	30.4 a	2.3 a	3.5 a	0.7	1.2 a
27	112 a	189 a	19.1 a	61.9 a	7.7 a	11.1 a	1.1	3.4 a
135	401 b	628 b	61.0 b	189 b	21.9 b	33.0 b	3.6	12.1 b
270	497 b	723 b	67.5 b	207 b	34.8 c	53.0 c	5.7	18.8 c

* < lower limit of quantitation
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level.

Tables 4.19a and b present the relationship between chemical soil characteristics (EC and pH) and concentration of REEs in roots and shoots of maize and oilseed rape in 2006. The correlation coefficients (r) values for the relationship between EC values and the La, Ce, Pr and Nd content in roots of maize were r= 0.69**, r= 0.73**, r= 0.79** and r= - 0.79** (Table 4.19a); for shoot concentrations the corresponding values were r= 0.71**, r= 0.76**, r= 0.76** and r= 0.87**. For oilseed rape, the correlation coefficients (r) values were also highly significant but less strong than in maize.

Table 4.19a: Correlation coefficients (r) for the relation between **concentration** of REEs in **maize** roots and soil pH and EC 66 days after sowing (2006) (n= 102)

		Roots				Soil pH	Soil EC
		La	Ce	Pr	Nd		
Roots	La	-	.88**	.93**	.93**	- .18	.69**
	Ce		-	.97**	.97**	- .18	.73**
	Pr			-	1.00**	- .25*	.79**
	Nd				-	- .25*	.79**
Soil pH						-	- .64**
Soil EC							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Table 4.19b: Correlation coefficients (r) for the relation between **concentration** of REEs in **maize** shoots and soil pH and EC 66 days after sowing in 2006 (n= 102)

		Shoots				Soil pH	Soil EC
		La	Ce	Pr	Nd		
Shoots	La	-	.83**	.99**	.99**	- .14	.71**
	Ce		-	.99**	.97**	- .22	.76**
	Pr			-	.99**	.45	.76**
	Nd				-	- .29	.87**
Soil pH						-	- .64**
Soil EC							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Chemical soil properties were not only related to REE concentrations in roots and shoots but also influenced the total uptake of these elements (Tables 4.20a and 4.20b). The same behavior of soil EC on the total uptake of REEs in roots and shoots of maize was determined (r= 0.28**, r= 0.31**, r= 0.64**, r= 0.62** and r= 0.33**, r= 0.42**, r= 0.42**, r= 0.63** for roots and shoots of maize, respectively). Similar results were determined for oilseed rape (see Appendix Tables B16a to B16d).

Table 4.20a: Correlation coefficients (r) for the relation between **uptake** of REEs for **maize** roots and soil pH and EC after 66 days of sowing in 2006 (n= 102)

		Roots				Soil pH	Soil EC
		La	Ce	Pr	Nd		
Roots	La	-	.27**	.51**	.51**	- .01	.28**
	Ce		-	.68**	.68**	.06	.31**
	Pr			-	.99**	- .20*	.64**
	Nd				-	- .18	.62**
Soil pH						-	- .64**
Soil EC							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Table 4.20b: Correlation coefficients (r) for the relation between **uptake** of REEs for **maize** shoots and soil pH and EC after 66 days of sowing (2006) (n= 102)

		Shoots				Soil pH	Soil EC
		La	Ce	Pr	Nd		
Shoots	La	-	.30**	.92**	.97**	.05	.33*
	Ce		-	.91**	.76**	- .09	.42**
	Pr			-	.91**	.32	.42
	Nd				-	- .26	.63**
Soil pH						-	- .64**
Soil EC							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

The relationship between Ca concentration in maize roots and REE concentrations in maize roots proved to be not significant. In contrast, these relationships were significant between REE concentrations in maize shoots and Ca concentrations in the same plant part (Figure 4.8).

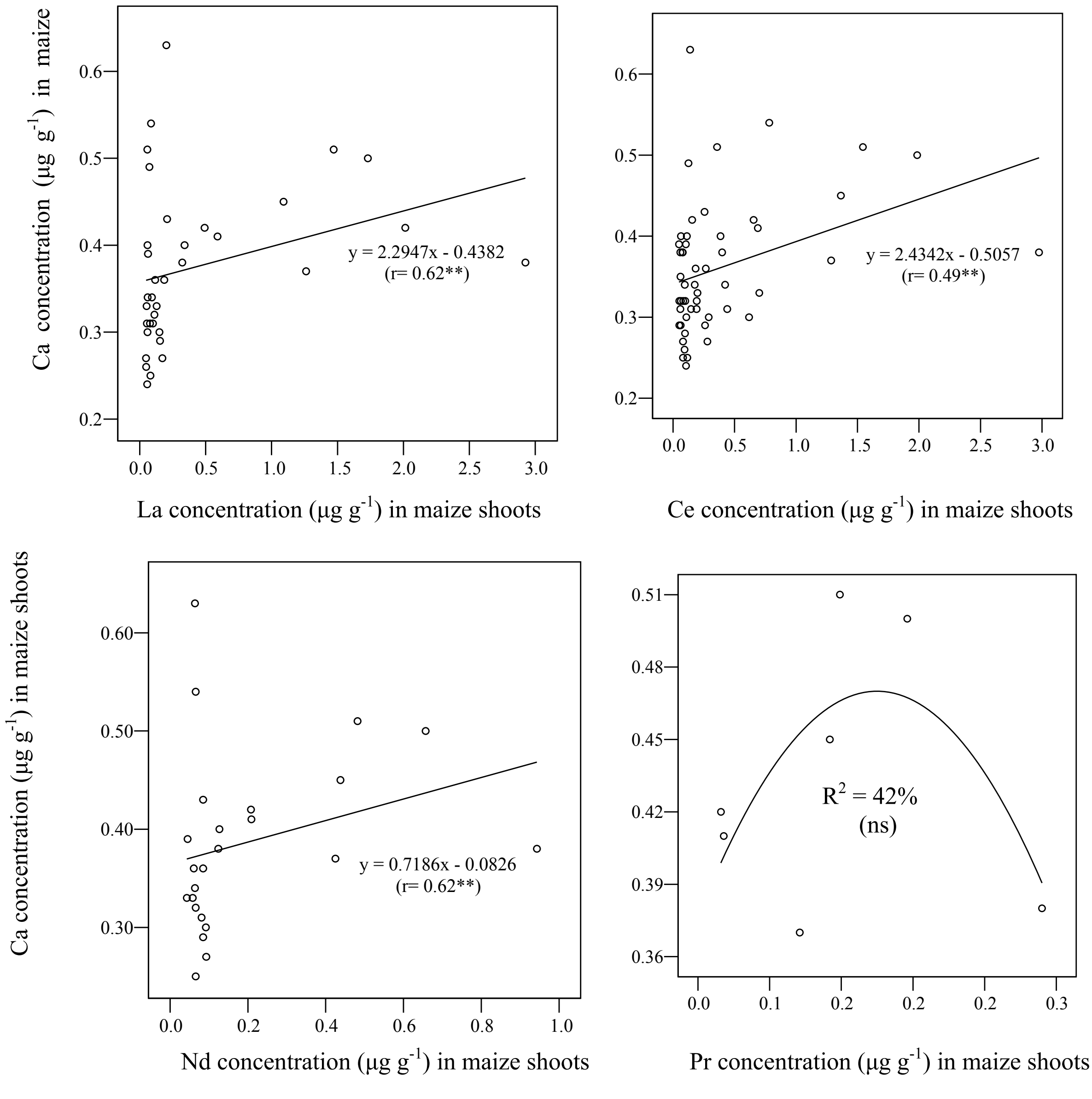


Figure 4.8: Relation between REE and Ca concentrations in maize shoots 66 days after sowing (2006) (Significance: *= $p < 0.005$, **= $p < 0.01$, ***= $p < 0.001$, ns= not significant)

Figure 4.9 illustrates the relationship between REE (La, Ce, Pr, and Nd) concentrations in roots and shoots of maize. This relationship proved to be highly significant for all elements as shown in the Figure 4.9. The high coefficients of correlation (r = 0.93**, r= 0.96**, r = 0.97** and r= 0.98** for Pr, Ce, Nd and La, respectively) reveal that translocation of REEs in above-ground plant parts depends on root uptake of these elements.

On average the La, Ce, Pr and Nd concentrations were about 100 times higher in roots than in shoots of maize.

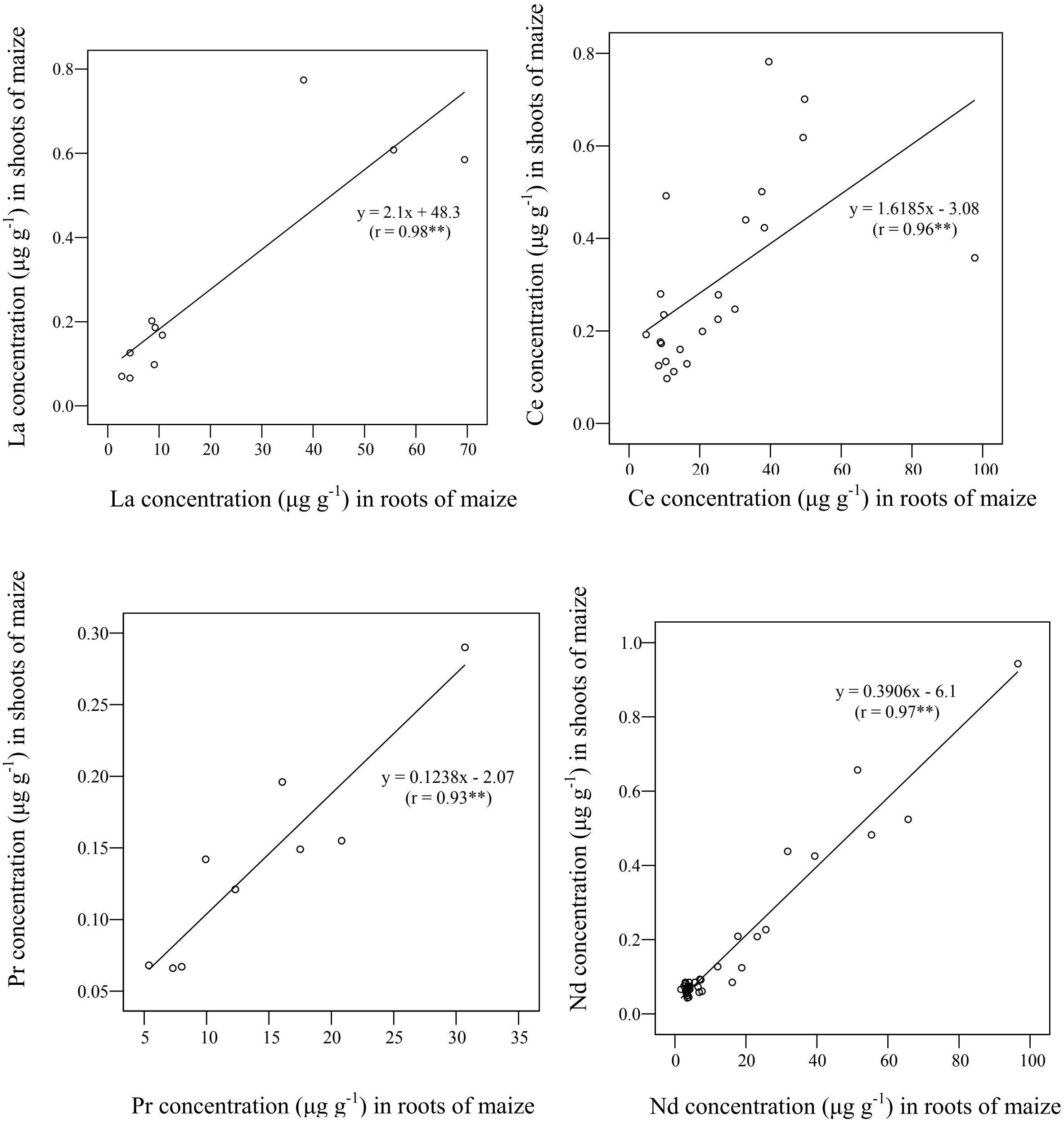


Figure 4.9: Relation between REE (La, Ce, Pr and Nd) concentrations in maize roots and shoots 66 days after sowing (2006) (Significance: *= $p < 0.005$, **= $p < 0.01$, ***= $p < 0.001$, ns= not significant)

Figure 4.10 illustrates the relationship between REE (La, Ce, Pr, and Nd) concentrations in roots and shoots of oilseed rape. Again close correlations were found for all elements, but these were less strong than for maize. The corresponding correlation coefficients (r) ranged from r= 0.81**, r= 0.89**, r= 0.92** and r= 0.95** for La, Pr, Ce, and Nd, respectively.

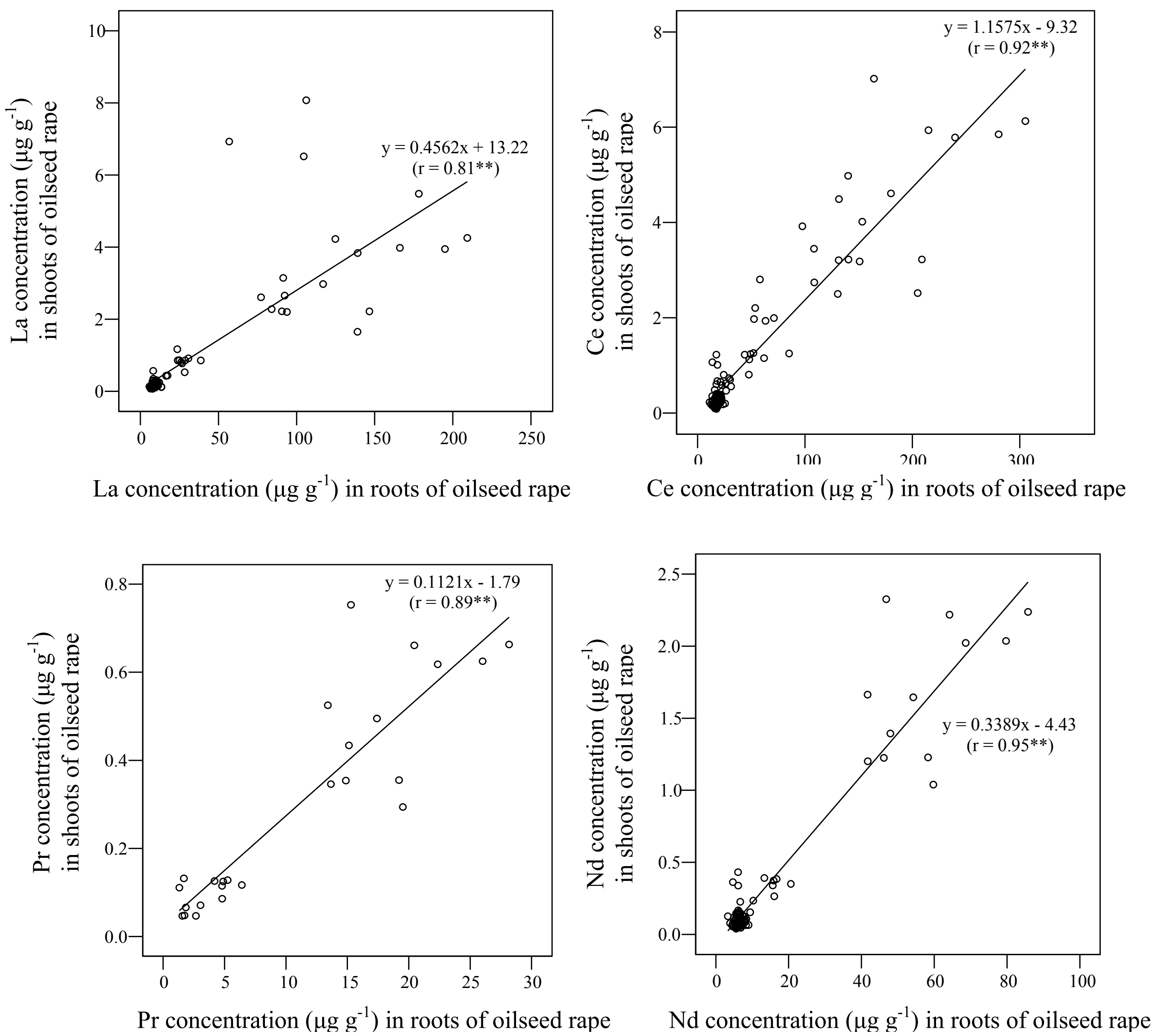


Figure 4.10: Relation between REE (La, Ce, Pr and Nd) concentrations of oilseed rape roots and shoots 66 days after sowing (2006) (Significance: *= $p < 0.005$, **= $p < 0.01$, ***= $p < 0.001$, ns= not significant)

Striking is the fact that the La and Ce concentrations in roots are more than three times higher in oilseed rape than in maize, while that of Pr and Nd cover the same range of concentration (Table 4.18 and Tables B.6 and B.7 in Appendix). Differences in the shoot concentrations between both crops are even more pronounced for Ca and Ce, which are about 10 times higher in oilseed rape than maize. The Pr and Nd concentration in oilseed rape shoots are about 27 and 2.5 times higher than in maize. The results reveal that crop and element-specific differences in root uptake of REEs exist and that translocation of individual REEs within the plant seem to be controlled by different transporter systems for oilseed rape and maize.

In the following section relationships between REE uptake in roots and shoots of maize and oilseed rape will be shown. Figure 4.11 illustrates the relationship between the uptake of REEs by maize roots and shoots. As before for the relationships for elemental concentrations, the relationships proved to be highly significant for the uptake of La, Ce, Pr and Nd, too. The corresponding correlation coefficients (r) for REE uptake of roots and shoots ranged from r= 0.68**, r= 0.77**, r= 0.88** and r= 0.89** for Pr, Ce, and Nd, La, respectively (Fig. 4.11).

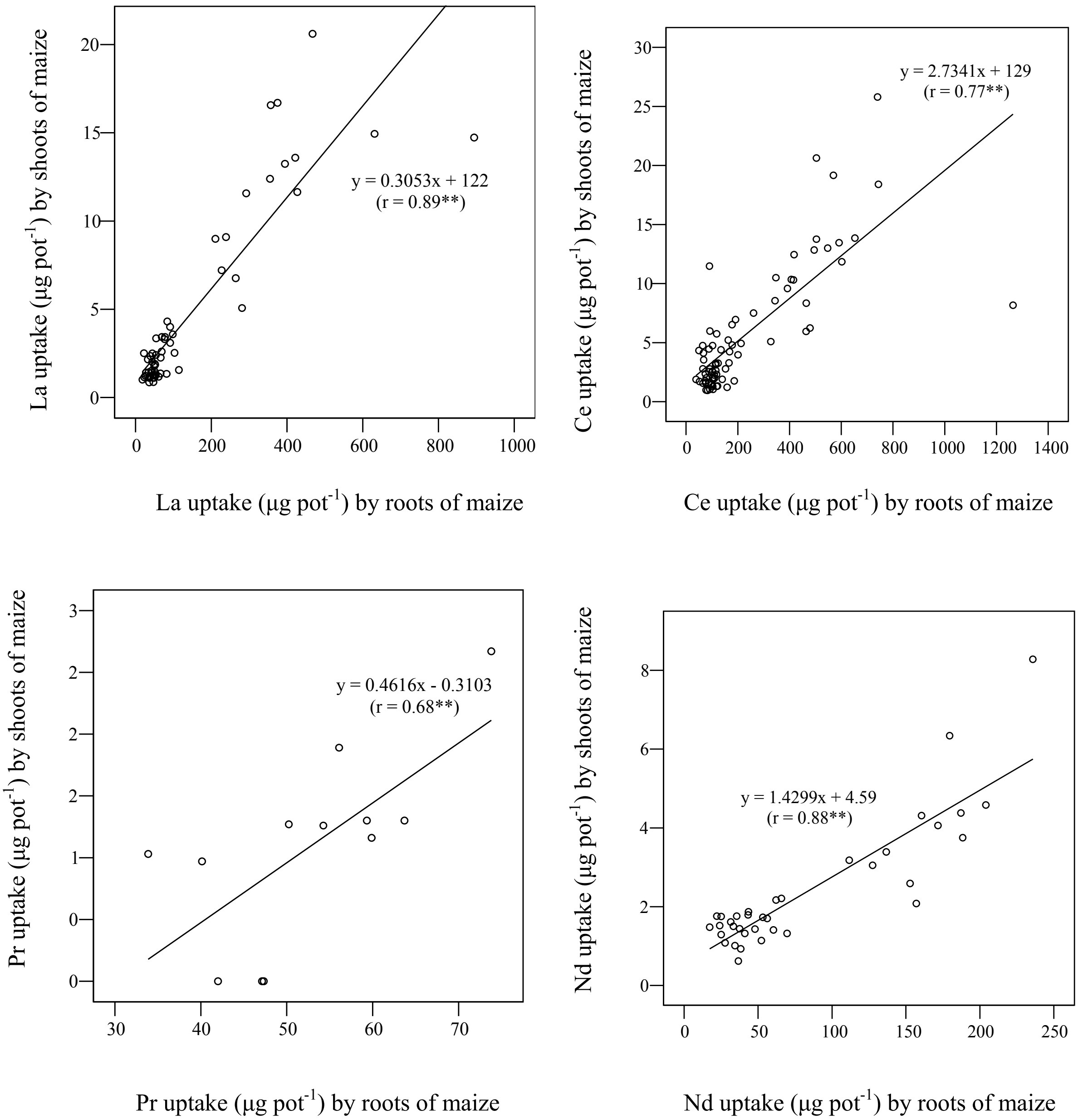


Figure 4.11: Relation between REE (La, Ce, Pr and Nd) uptake by maize roots and shoots 66 days after sowing (2006) (Significance: *= p < 0.005, **= p < 0.01, ***= p < 0.001, ns= not significant)

Figure 4.12 illustrates the relationship between REE uptake by roots of oilseed rape and uptake of REEs in shoots of oilseed rape. The corresponding correlation coefficients (r) ranged from 0.77**, 0.81, 0.85** and 0.87** for Pr, La, Nd and Ce, respectively.

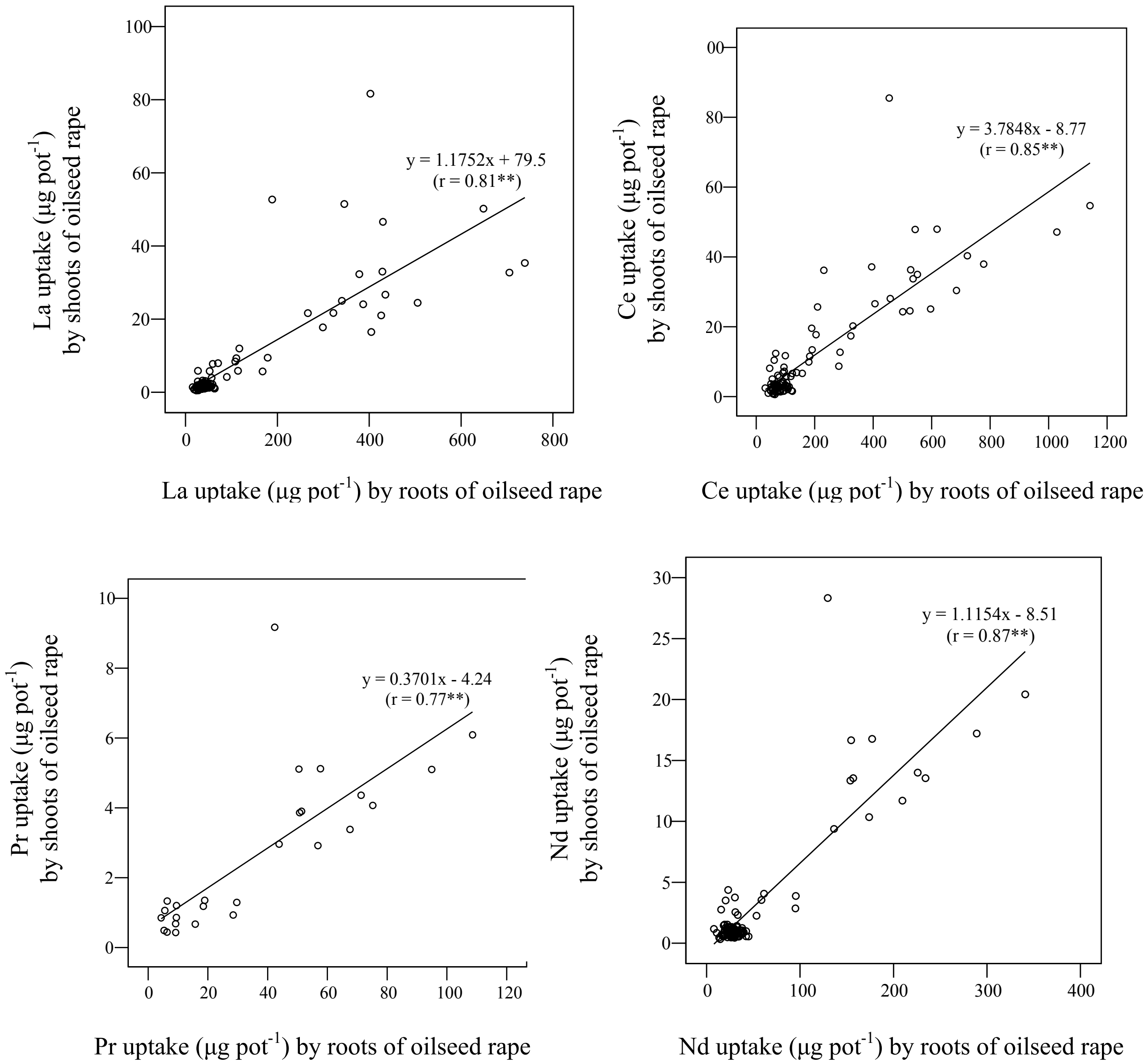


Figure 4.12: Relation between REE (La, Ce, Pr and Nd) uptake by oilseed rape roots and shoots 66 days after sowing (2006) (Significance: *= $p < 0.005$, **= $p < 0.01$, ***= $p < 0.001$, ns= not significant)

Effect of REE application on concentrations of essential nutrients in roots and shoots of maize and oilseed rape

In this section only the results for the effect of graded REE-fertilizer rates on the concentration and uptake of essential plant nutrients by maize and oilseed rape is shown as they delivered the strongest effect. Results for the impact of graded La and Ce applications are summarized in Tables B.17 to B.24 in the Appendix.

The plant tissue concentrations of the essential nutrients S, K, Ca, Mg, Fe, Mn, Zn, Cu and B were analyzed 35 and 66 days after sowing in the treatment with graded REE-fertilizer applications (Tables 4.21a and b). In general, in case of roots, higher concentrations of K, Ca, and Mg were found for maize than oilseed rape. In comparison, in roots of oilseed rape higher values of S, Fe, Mn, Zn, Cu, and B were found. The values of K, Ca and Mg concentrations of maize roots ranged from (1.07-1.67%), (0.69-0.86%), and (0.33-0.41%); K, Ca and Mg concentrations ranged from 0.87-1.04%, 0.53-0.62%, and 0.16-0.19% in roots of oilseed rape. The values of S, Fe, Mn, Zn, Cu, and B concentrations of oilseed rape roots were (0.27 - 0.31%), (3655.1-5400.3 µg g^{-1}), (672.7-1114.2 µg g^{-1}), (95.2-139.8 µg g^{-1}), (33.8-41.3 µg g^{-1}) and (17.3-26.2 µg g^{-1}), respectively, whereas (1.79-2.10%), (2318.9-3489.4 µg g^{-1}), (465.2-682.0 µg g^{-1}), (46.0-83.7 µg g^{-1}), (14.3-19.3 µg g^{-1}) and (13.16.2 µg g^{-1}) in case of roots of maize.

Table 4.21a: Influence of graded REE-fertilizer application rates on mean of essential nutrients concentration in roots and shoots of **maize** 66 days after sowing (2006)

REE-fertilizer application rates (µg g^{-1})	**Roots of maize**								
	S	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
	--------------(%)-----------				**-------------(µg g^{-1})----------------**				
0	0.18 a	1.67 b	0.69 a	0.33 a	2618 ab	465 a	46.0 a	16.2 ab	10.7 a
2.7	0.19 a	1.64 b	0.86 b	0.36 a	2318 a	512 ab	49.2 a	14.7 a	13.6 b
27	0.18 a	1.07 a	0.80 ab	0.36 a	3215 bc	607 ab	75.3 ab	14.3 a	15.4 bc
135	0.19 a	1.08 a	0.81 ab	0.41 a	3255 bc	682 b	60.5 b	15.2 ab	14.7 bc
270	0.21 a	1.28 a	0.73 ab	0.39 a	3489 c	560 ab	83.7 b	19.3 a	16.2 c
	Shoots of maize								
0	0.14 ab	2.86 ab	0.49 a	0.16 a	54.7 a	269 a	76.0a b	11.0 b	11.1
2.7	0.11 a	1.70 a	0.34 a	0.15 a	165 b	204 a	74.5 ab	6.0 a	10.3
27	0.10 a	1.72 a	0.39 a	0.15 a	160 b	211 a	63.0 ab	7.3 a	10.3
135	0.13 ab	2.42 a	0.34 a	0.13 a	192 b	269 a	58.7 a	7.5 a	10.6
270	0.17 b	4.06 b	0.48 a	0.15 a	201 b	329 a	91.5 b	8.3 ab	9.6

All values of B of maize shoots below lower limit of the quantitation
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

In case of shoots, in general, the highest concentration values of K, Fe, and Cu were found in shoots of maize, whereas in shoots of oilseed rape the highest values of S, Ca, Mg, Mn, Zn and B were determined. The values of K, Fe and Cu concentrations of maize shoots ranged from (1.70-4.06%), (54.7-201.4 µg g^{-1}), and (6.0-11.0 µg g^{-1}), and in oilseed rape shoots the corresponding values were (2.94-3.22%), (62.9-181.1 µg g^{-1}) (7.2-8.6 µg g^{-1}). The values of S, Ca, Mg, Mn, Zn, B concentrations of oilseed rape shoots were (0.32-0.39%), (1.13-1.23%), (0.18-0.22%), (518.0-772.3 µg g^{-1}), (60.2-94.0 µg g^{-1}) and (11.3-13.4 µg g^{-1}), respectively; in maize shoots the corresponding values were (0.10-0.17%), (0.34-0.49%), (0.13-0.16%), (204.0-329.0 µg g^{-1}), (58.7-91.5 µg g^{-1}) and (9.6-11.1 µg g^{-1}).

In case of maize, with increasing application rates of REE-fertilizer the concentration of all essential macro and micro-nutrients in roots (except K) increased, whereas in shoots the concentration of Ca, Mg, Cu, and B were decreased and the concentration of K, S, Zn, Mn and Fe increased with REE-fertilizer application. In case of oilseed rape, the results were different. The concentrations of S, Ca, Mn, Cu, and Zn in roots increased with increasing rates of REE-fertilizer application, whereas the concentration of K, Mg, Fe, and B decreased. In case of shoots of oilseed rape, increasing concentrations of S, Mn, and B were analyzed, while the K, Ca, Mg, Fe, Zn, and Cu decreased with increasing the REE-fertilizer application (Tables 4.21a and b).

Table 4.21b: Influence of graded REE-fertilizer application rates on mean of essential nutrients concentration in roots and shoots of **oilseed rape** 66 days after sowing (2006)

REE-fertilizer application rates (µg g^{-1})	**Roots of oilseed rape**								
	S	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
	--------------(%)-----------				--------------(µg g^{-1})-----------------				
0	0.28 a	1.04 a	0.53 a	0.19 ab	5312 a	672 a	95.2a	33.8 a	24.0 bc
2.7	0.27 a	0.89 a	0.62 a	0.19 b	5400 a	825 ab	123 ab	40.3 a	26.2 c
27	0.29 a	0.87 a	0.57 a	0.18 ab	4936 a	878 ab	112 ab	41.8 a	26.0 c
135	0.31 a	0.89 a	0.62 a	0.19 b	4748 a	838 ab	110 ab	38.3 a	22.9 b
270	0.31 a	0.89 a	0.58 a	0.16 a	3955 a	1114 b	139 b	40.5 a	17.3 a
	Shoots of oilseed rape								
0	0.32 a	3.22 a	1.23 a	0.22 a	181 b	518 a	94.0 b	8.6 a	11.3 a
2.7	0.32 a	2.94 a	1.14 a	0.19 a	62.9 a	498 a	60.2 a	7.2 a	12.7 a
27	0.39 a	3.21 a	1.13 a	0.18 a	75.6 a	647 ab	76.5 ab	8.2 a	13.4 a
135	0.35 a	2.95 a	1.23 a	0.21 a	92.6 a	608 ab	67.3 a	8.0 a	13.3 a
270	0.37 a	3.08 a	1.13 a	0.18 a	98.0 a	772 b	73.3 ab	8.0 a	13.1 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

As mentioned before, the REE content of roots and shoots increased with increasing REE-fertilizer application (Tables 4.18a and b) and the highest concentration of REEs was found in roots when compared to shoots of oilseed rape and maize. It was also found that accumulation of REEs in different parts of plants decreased in the following order: root > shoots and REEs in the order: Ce > La > Nd >Pr for each plant part and for each crop. From Tables 4.21a and b, it can be concluded that the concentration of macro and micro-nutrients decreased in shoots of maize and oilseed rape in the order of K > Ca > S > Mg and Mn> Fe > Zn > B >Cu. In case of roots, the concentrations decreased in the order K > Mg > Ca > S and Mn > Fe > Zn > Cu > B for both crops.

From the results obtained it can be concluded that with increasing doses of REE-fertilizer the concentration of REE (La, Ce, Pr, and Nd) increased in both roots and shoots of maize and oilseed rape. This means that graded REE-fertilizer applications yielded a pronounced effect on the REE content of different plant parts. The magnitude of this effect varied in relation to REE species (La, Ce, Pr, Nd), plant species (maize or oilseed rape) and plant part (shoots or roots). In general, graded REE-fertilizer applications increased the concentration of essential nutrients in roots of maize (except K). This trend was not consistent for oilseed rape. With increasing graded REE-fertilizer application rates, the concentrations of K, Fe, and Zn, decreased for shoots of both maize and oilseed rape.

Correlation analysis for essential nutrients in roots and shoots of maize and oilseed rape and some chemical properties (soil pH and EC) was carried out (see Appendix Tables B.29 and B.34). In case of maize roots, all essential nutrients were correlated negatively with soil pH. Soil EC correlated positively with all elements, except Mg (r= - 0.13) and K (r= - 0.09). In case of oilseed rape, the relationship between soil pH and essential nutrients in roots was negative for all elements except S (r= 0.28**). Soil EC correlated positively with all elements, except Mg (r= - 0.28**), Ca (r= - 0.30**) and K (r= - 0.38**) in case of shoots of oilseed rape and Mg, Ca, K, and B (r= - 0.30**) in case of roots of oilseed rape.

Tables B.29 to B.34 (Appendix) show the correlation analysis for La, Ce, Pr, Nd and essential plant nutrients in roots and shoots of oilseed rape and maize. In the case of oilseed rape, the correlation coefficients (r) for the relationships between essential plant nutrients and individual REEs in roots revealed that there was a significant and negative correlation only for Fe and La (r= - 0.27**), Ce (r= - 0.32**), Pr (r= - 0.38**) and Nd (r= – 0.37**), and B and La (r= - 0.051**), Ce (r= - 0.52**), Pr (r= - 0.56**), and Nd (r= – 0.56**) (Table B.31 in Appendix). In case of shoots of oilseed rape, these relationships were negative for K, Ca, Mg and Fe and La, Ce, Pr and Nd, and positive for S, Cu, Mn, Zn, and B and La, Ce, Pr and Nd.

In case of roots of maize, only K and Ca showed a negative relationship with La, Ce, Pr and Nd, whereas all other essential nutrients had a positive relationship (Table B.30 in Appendix). This positive relationship for K and La, Ce, Pr and Nd was highly significant with correlation coefficients between r= 0.78** to r= 0.88**.

Figure 4.13 shows the relationship between B concentrations in roots of oilseed rape and concentration of REEs in shoots of oilseed rape. The correlation coefficients (r) ranged from r= -0.38**, r= -0.55** to r=-0.62** for Ce, La, and Nd, respectively.

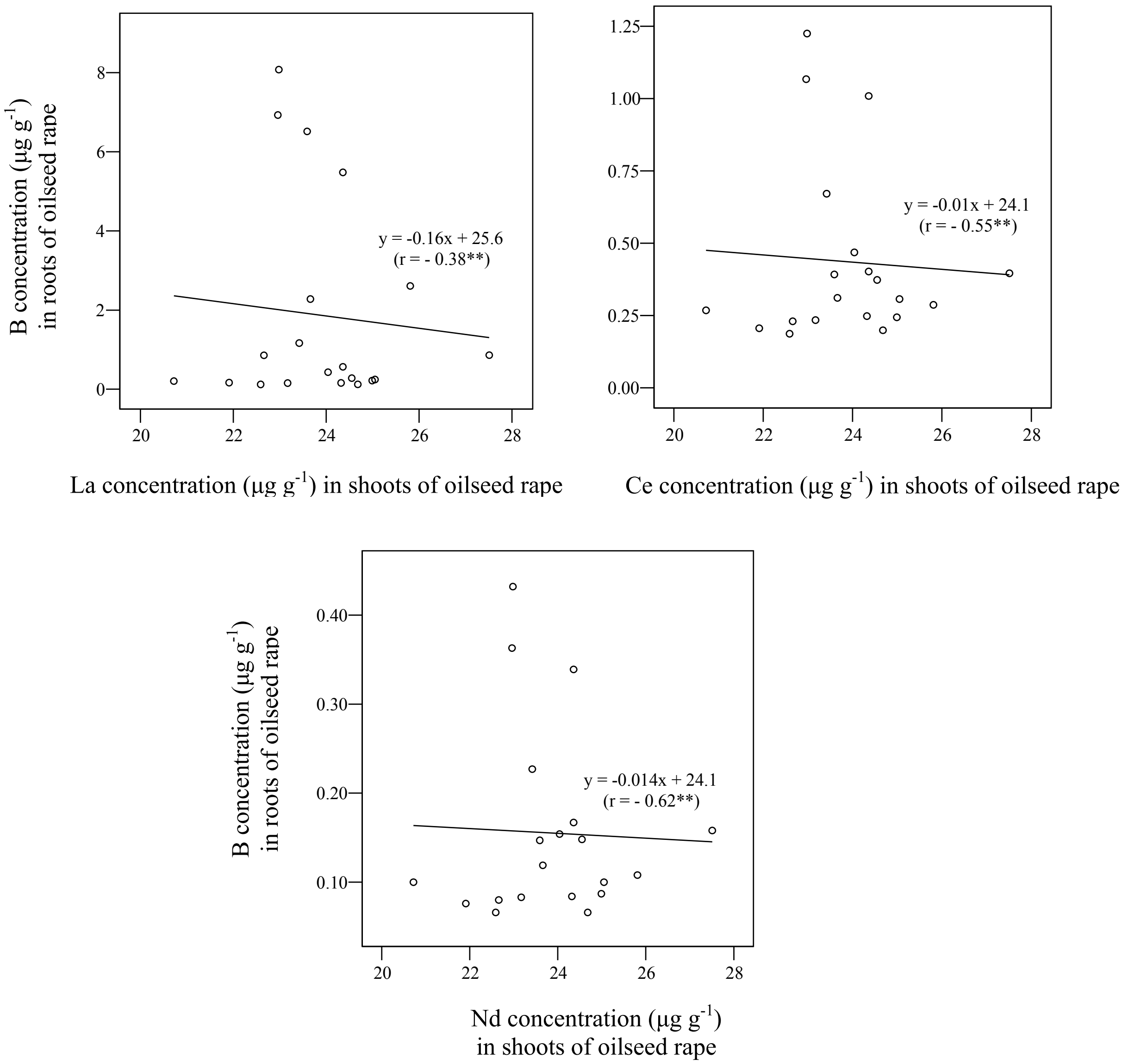


Figure 4.13: Relation between B concentration in oilseed rape roots and REE (La, Ce and Nd) concentrations in oilseed rape roots and shoots 66 days after sowing (2006)
(Significance: *= $p < 0.005$, **= $p < 0.01$, ***= $p < 0.001$, ns= not significant)

Effect of REE application on uptake of essential nutrients

It was the aim of this section to determine the influence of REE applications on the uptake of essential macro and micro-elements. The plant uptake of the essential nutrients S, K, Ca, Mg, Fe, Mn, Zn, Cu and B was analyzed 66 days after sowing and results are summarized in Tables from 4.22a and b and Tables B.25 to B.28 (Appendix).

As previous results showed increasing REE-fertilizer application rates significantly affected the concentration of all essential nutrients in case of maize roots, while the uptake of Ca, Mg and Mn by maize shoots was not significantly influenced (Table 4.21a). In case of oilseed rape, graded REE application rates significantly decreased the S, K and B uptake of roots (Table 4.22b). In general, there was no significant effect of La and Ce application rates on the uptake of essential plant nutrients in roots and shoots of oilseed rape (see Tables B.25 to B.28 in Appendix). In general, the uptake of essential macro and micro-nutrients decreased with increasing of REE-fertilizer application rates.

In case of roots, the highest uptake values were found for all essential macro and micro-nutrients in maize, whereas that for oilseed rape were least affected by graded REE-fertilizer application rates. Inverse results were determined for shoots where the S, Ca and Mn uptake was highest for oilseed rape and distinctly lower in maize (Tables 4.22a and b).

Table 4.22a: Influence of graded REE-fertilizer application rates on the mean **uptake** of essential nutrients by roots and shoots of maize 66 days after sowing (2006)

REE-fertilizer application rates (µg g^{-1})	**Uptake by roots of maize**								
	S	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
	Uptake (mg pot^{-1})							**Uptake (µg pot^{-1})**	
0	18.2 b	171 b	68.5 bc	32.0 b	26.4 b	4.6 b	0.45 ab	161 c	107 b
2.7	19.4 b	165 b	86.1 b	35.7 b	23.8 b	5.2 b	0.49 bc	149 bc	138 b
27	15.8 b	89.9 a	70.6 bc	31.9 b	28.5 b	5.4 b	0.66 c	126 bc	135 b
135	14.5 b	84.9 a	62.6 c	31.0 b	25.2 b	5.1 b	0.46 ab	115 b	113 b
270	7.7 a	49.9 a	28.8 a	15.2 a	13.3 a	2.4 a	0.31 a	70.2 a	62.2 a
	Uptake by shoots of maize								
	Uptake (mg pot^{-1})							**Uptake (µg pot^{-1})**	
0	23.5 bc	470 a	80.8 b	27.0 b	0.9 a	4.4 a	1.3 a	181 b	-----*
2.7	22.8 ab	355 a	72.8 ab	31.9 b	3.4 bc	4.3 a	1.6 a	128 ab	-----*
27	23.0 ab	383 a	87.3 b	31.9 b	3.6 c	4.8 a	1.4 a	160 b	-----*
135	25.2 b	466 a	67.3 ab	26.4 b	3.9 c	5.3 a	1.2 a	146 b	-----*
270	15.7 a	358 a	44.2 a	13.9 a	1.9 ab	3.2 a	0.9 a	77.8 a	-----*

* < lower limit of quantitation
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Table 4.22b: Influence of graded REE-fertilizer application rates on the mean **uptake** of essential nutrients by roots and shoots of oilseed rape 66 days after sowing (2006)

REE-fertilizer application rates (µg g^{-1})	**Uptake by roots of oilseed rape**								
	S	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
	Uptake (mg pot^{-1})							**Uptake (µg pot^{-1})**	
0	12.4 b	1.04 b	25.6 a	8.40 a	23.6 a	3.0 a	0.42 a	149 a	106 b
2.7	10.6 ab	0.89 ab	24.6 a	7.85 a	22.0 a	3.3 a	0.49 a	156 a	104 b
27	10.0 ab	0.87 a	21.7 a	6.81 a	18.5 a	3.2 a	0.39 a	144 a	95.2 b
135	11.9 ab	0.89 ab	23.2 a	7.54 a	18.9 a	3.2 a	0.43 a	146 a	90.7 ab
270	9.15 a	0.89 a	16.7 a	5.20 a	12.8 a	2.7 a	0.41 a	121 a	53.5 a
	Uptake by shoots of oilseed rape								
	Uptake (mg pot^{-1})							**Uptake (µg pot^{-1})**	
0	30.5 a	288 a	112 a	20.2 a	1.6 b	4.6 a	0.80 b	76.9 a	97.3 a
2.7	31.5 a	290 a	112 a	19.5 a	0.6 a	4.9 a	0.60 a	68.8 a	125 a
27	37.6 a	309 a	110 a	18.2 a	0.7 a	6.2 ab	0.70 ab	80.6 a	129 a
135	32.1 a	269 a	113 a	19.1 a	0.8 a	5.5 ab	0.60 a	74.9 a	122 a
270	34.8 a	288 a	105 a	17.1 a	0.9 a	7.2 b	0.70 ab	76.5 a	116 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

The results of the correlation analysis for the parameters soil pH, EC and the uptake of essential nutrients by roots and shoots are shown in Tables B.35 to B.37 in the Appendix. A highly negative, significant statistical correlation was found for the relationship between soil EC and the uptake of all essential macro and micro-nutrients; correlation coefficients ranged from r= - 0.34** to r= – 0.83** when maize roots were analyzed (Table B.35 in Appendix). For the shoots of maize, the previous relationships were also negative but less strong than for roots (except B). The results for oilseed are summarized in Table B.36. Also, a negative, significant statistical correlation was found for the relationship between soil EC and the uptake of all essential micro- and micro-nutrients; correlation coefficients ranged from r= - 0.31** to r= – 0.62** when oilseed rape roots were analyzed. The only negative and significant relationships were found between soil EC and Ca (r= - 0.23*) and Mg (r= - 0.26*) in shoots of oilseed rape. In comparison, the relationships between soil pH and essential plant nutrients were negative and non-significant, except for Cu and Fe where they were positive.

Soil/plant transfer of REEs

In this section the results for the effect of graded REE-fertilizer rates on the transfer of REEs from soil to plant are shown as exclusively as they delivered the strongest effect. Results for the impact of graded La and Ce applications on transfer factors$_{soil/plant}$ (TFs) are summarized in Tables B.38 – B.41 in the Appendix.

The ratio of the REE concentrations (La, Ce, Pr and Nd) in plant tissues in relation to their content in the soil is defined as the transfer factor (TF). The soil/plant transfer of REEs depends on plant species and environmental conditions. Generally, low transfer factors of 0.04 to 0.09 were determined for REEs (Tyler, 2004), indicating low uptake of REEs in above-ground plant parts. Even lower TFs of 0.02 to 0.03 were reported by Krafka (1999).

In the present study, the transfer factor (TF, µg µg^{-1}) was calculated by using the following formula: $TF_{soil/plant} = C_{Plant}/C_{Soil}$, where C_{Plant} reflects the total concentration of individual REEs (La, Ce, Pr, and Nd) in plants. Values for C_{Soil} reflect the plant available background concentration plus the rate of REEs added to the soils in different treatments. For the individual REEs, the concentrations of La, Ce, Pr, and Nd in soil were 1.0, 0.8, 0.2 and 0.7 g µg^{-1}, respectively. For the sum of REEs the TF of roots or shoots (total TF_{roots} or total TF_{shoots}) was calculated by adding up the concentration of REEs (La, Ce, Pr, and Nd) in roots and shoots; these values were divided by the sum of plant available REEs in soil (2.7 g µg^{-1}) plus the amount of REEs added to the soil.

In Tables 4.23a and 4.23b mean TFs for the transfer of REEs from soil to roots and shoots of oilseed rape and maize in relation to different treatments were calculated. The results showed that for the sum of REEs (La, Ce, Pr and Nd) the TFs were expectedly higher for roots than shoots. The transfer into roots and shoots was clearly higher for oilseed rape than of maize. Table 4.24 shows the effects of graded REEs applications on TFs (µg μg^{-1}) of individual REEs and the sum of REEs in roots and shoots of oilseed rape as an averaged effect over all treatments.

As mentioned before, increased REE concentrations in roots and shoots following the application of REE-fertilizer were determined (see Tables 4.18a and b). However, the individual TF of REEs decreased with increasing doses of REE-fertilizer in roots and shoots, for both maize and oilseed rape (Tables 4.23a and b). In general, for individual REEs the TF values decreased in the order Ce > La ≥ Nd ≥ Pr in roots and shoots of oilseed rape and maize. The total TF of roots or shoots decreased with increasing of graded REE-fertilizer application rates for both maize and oilseed rape. In general, the TF values (individual and total) of oilseed rape were higher than of maize for both, roots and shoots.

Table 4.23a: Influence of graded REE-fertilizer application rates on the mean of transfer factors (**TF,** µg μg^{-1}) of individual REEs and the sum of REEs (total) in roots and shoots of **maize** 66 days after sowing (2006)

REE-fertilizer application rates (µg g^{-1})	**Individual TF (µg μg^{-1}) for roots of maize**				**Total TFroots**
	La	**Ce**	**Pr**	**Nd**	
0	4.24 c	11.0 c	4.47 c	4.67 c	6.39 c
2.7	2.36 b	6.14 b	2.54 b	2.59 b	3.56 b
27	0.92 a	2.24 a	0.91 a	0.89 a	1.29 a
135	0.67 a	1.42 a	0.57 a	0.53 a	0.85 a
270	1.19 a	2.23 a	0.88 a	0.80 a	1.38 a
	Individual TF (µg μg^{-1}) for shoots of maize				**Total TFshoots**
0	0.096 b	0.283 b	-----*	0.084	0.142 c
2.7	0.031 a	0.054 a	-----*	0.047	0.026 b
27	0.014 a	0.027 a	-----*	0.010	0.016 ab
135	0.008 a	0.013 a	0.007	0.005	0.008 a
270	0.017 a	0.022 a	0.009	0.008	0.015 ab

* < lower limit of quantitation.
For values, which have no letters ANOVA could not be run because of limited cases
Individual TF= (total element content in plant)/(Plant available content of element + added REE at different rates) Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Striking is that the TF for La decreases less strong with increasing REE fertilizer rates in maize roots than shoots, while in case of oilseed rape a similar decrease was determined for both plant organs. With increasing REE fertilizer rate a distinct increase of the TF was found in shoots compared to roots for Ce and Nd in maize, Pr in oilseed rape.

Table 4.23b: Influence of graded REE-fertilizer application rates on mean of transfer factors (**TF,** µg µg^{-1}) of individual REEs and the sum of REEs (total) in roots and shoots of **oilseed rape** 66 days after sowing (2006)

REE-fertilizer application rates (µg g^{-1})	**Individual TF (µg µg^{-1}) for roots of oilseed rape**				**Total TFroots**
	La	**Ce**	**Pr**	**Nd**	
0	9.54 c	23.9 c	9.44 c	9.68 c	13.8 c
2.7	5.60 b	13.1 b	5.25 b	5.25 b	7.71 b
27	2.72 a	5.74 a	2.29 a	2.12 a	3.43 a
135	2.04 a	3.96 a	1.54 a	1.36 a	2.39 a
270	1.62 a	2.92 a	1.08 a	0.95 a	1.79 a
	Individual TF (µg µg^{-1}) for shoots of oilseed rape				**Total TFshoots**
0	0.225 b	0.468 b	0.511	0.182 b	0.277 a
2.7	0.116 ab	0.222 ab	0.176	0.087 ab	0.134 ab
27	0.072 a	0.129 a	0.053	0.046 a	0.080 a
135	0.049 a	0.092 a	0.040	0.038 a	0.058 a
270	0.037 a	0.070 a	0.031	0.029 a	0.044 a

For values, which have no letters ANOVA could not be run because of limited cases
Individual TF= (total element content in plant)/(Plant available content of element + added REE at different rates). Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Graded REE-fertilizer application rates resulted in the highest transfer of REEs in roots and shoots of maize and oilseed rape (as an averaged effects over all treatments) (Table 4.24). In comparison, graded applications of Ca resulted in the highest values for the TFs for the sum of REEs for maize and oilseed rape roots and the lowest values for individual REEs. This effect was not fond in shoots.

Table 4.24: Influence of graded REE applications on TFs (µg µg^{-1}) of individual REEs and sum of REEs in roots and shoots of oilseed rape 66 days after sowing (2006) (averaged effects over all treatments)

Treatments	**Individual TF of roots**				**TF total**	**Individual TF of shoots**				**TF total**
	La	**Ce**	**Pr**	**Nd**		**La**	**Ce**	**Pr**	**Nd**	
	Maize									
Control	4.24 b	11.0 b	4.48 b	4.68 b	13.8 b	0.096 b	0.283 b	----*	0.084 c	0.277 b
Lanthanum	0.97 a	1.61 a	0.66 a	0.68 a	4.7 a	0.015 a	0.016 a	----*	0.051 b	0.132 a
Cerium	0.62 a	2.08 a	0.68 a	0.70 a	4.4 a	0.015 a	0.034 a	----*	0.019 a	0.087 a
REE-fertilizer	1.29 a	3.01 a	1.23 a	1.20 a	3.8 a	0.016 a	0.029 a	0.008	0.009 a	0.079 a
Calcium	0.65 a	1.73 a	0.71 a	0.73 a	12.1 b	0.028 a	0.022 a	----*	0.004 a	0.156 a
	Oilseed rape									
Control	9.54 b	23.9 b	9.44 b	9.68 b	6.39 b	0.225 c	0.469 b	0.511	0.182 b	0.142 b
Lanthanum	2.68 a	3.89 a	1.56 a	1.59 a	1.85 a	0.098 b	0.092 a	0.033	0.037 a	0.023 a
Cerium	1.32 a	4.35 a	1.31 a	1.35 a	2.08 a	0.029 a	0.086 a	-----*	0.018 a	0.017 a
REE-fertilizer	2.99 a	6.44 a	2.54 a	2.42 a	1.77 a	0.068 ab	0.128 a	0.048	0.050 a	0.016 a
Calcium	1.29 a	3.22 a	1.29 a	1.35 a	7.26 b	0.021 a	0.038 a	-----*	0.015 a	0.048 a

*< lower limit of quantitation
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level
TF_{total}= (La, Ce, Pr, and Nd content in plant)/(La, Ce, Pr, and Nd content in soil + La, Ce, Pr, and Nd added)

4.3.3 Influence of REEs on stress-related enzyme activities in maize and oilseed rape

Many environmental and genetic factors may affect the levels of the active principles of plant material (e.g. Laasonen et al., 2002) and both biotic and abiotic stress exert a considerable influence on the levels of secondary metabolites in plants, the synthesized metabolites being typically involved in defense responses of plants (Montanari et al., 2008). Most biotic and abiotic stresses (heat stress, desiccation, osmotic shock, freezing disease, insect, pathogen, temperature, drought, salinity, anaerobe, etc.) faced by plants were related to environmental conditions (Li et al., 2008). Under abiotic stresses, the accumulation of osmo-protectants (compatible solutes) is a common response observed in the plant kingdom (Luo et al., 2008).

The activities of several enzymes involved in plant protection against stress are important for studying the eco-physiology of plants. Plants have a large battery of enzymes that aid in their defense against adverse environmental conditions and attack by other organisms. They are glutathione *S*-transferase, glutathione reductase (GR), ascorbic acid peroxidase (APOX), catalase (CAT) and superoxide dismutase (SOD). APOX and CAT are both involved in regulating H_2O_2 concentrations, and SOD scavenges superoxide radicals, resulting in protection of the plant against those chemical species, and are included as part of an 'antioxidant network' (Davis and Swanson, 2001).

As mentioned before, changes in both activity and content of several plant enzymes have been observed in plants treated with REEs and therefore considered as possible explanations for the effects of REEs on plants. To investigate and evaluate stress-related enzyme activities and the toxic effects of REEs, leaf discs from maize and oilseed rape were analyzed. α-Tocopherol and total chlorophyll in leaf discs for both crops were determined. The effects of graded REE application rates (La, Ce, REE-fertilizer) on both α–tocopherol and total chlorophyll in leaves of maize and oilseed rape are summarized in Table 4.25. The results clearly reveal that oilseed rape plants contained the highest values of both α–tocopherol and total chlorophyll. Graded REE-fertilizer application rates increased the α-tocopherol content in maize and oilseed rape leaves, but this effect was not significant (Table 4.25).

In general, the total chlorophyll content in maize and oilseed rape leaves decreased with increasing REE application rates (La, Ce, REE-fertilizer) as shown in Table B.42 (see Appendix). A non-significant negative relationship between total chlorophyll content in leaves of oilseed rape and concentration of REEs (La, Ce, Pr, and Nd) was found in both roots and shoots of oilseed rape. The relationship between total chlorophyll content in maize leaves and concentration of REEs in both roots and shoots of maize was positive. The only correlation coefficient, which was significant (r= 0.85*) was that for the relationship between chlorophyll content and Pr concentration in shoots of maize.

The relationship between α-tocopherol in maize and oilseed rape leaves and the concentration of REEs in both roots and shoots was positive, however, not significant (Table B.43 in Appendix).

Non-significant increasing in α-tocopherol content in both maize and oilseed rape leaves with increasing of REE-fertilizer application rates as shown in Table 4.26. In general, the total chlorophyll content in maize and oilseed rape leaves decreased with increasing of REE application rates as shown in Table B.32 (see Appendix). It was found non-significant negative correlated relationship between total chlorophyll content in leaves of oilseed rape and concentration of REEs (La, Ce, Pr, and Nd) in both roots and shoots of oilseed rape. The (r) values ranged from (- 0.20 to – 0.52). The correlated relationship between total chlorophyll content in maize leaves and concentration of REEs in both roots and shoots of maize was positive. The only (r) value which was significant (r= 0.85*) in case of concentration of Pr in shoots of maize.

The relationship between α-tocopherol in maize and oilseed rape leaves and the concentration of REEs in both roots and shoots was positive, however, not significant (Table B.43 in Appendix). Increasing rates of REE-fertilizer did not significantly increase the α-tocopherol content in both maize and oilseed rape leaves (Table 4.26).

Table 4.25: Influence of rated REE applications on α-tocopherol ($\mu g\ g^{-1}$ DW) and total chlorophyll ($\mu mol\ g^{-1}$ DW) in leaf discs of maize and oilseed rape 66 days after sowing (2005) (averaged effects over all treatments)

Treatments	Maize		Oilseed rape	
	α-Tocopherol ($\mu g\ g^{-1}$ DW)	**Total chlorophyll ($\mu mol\ g^{-1}$ DW)**	**α-Tocopherol ($\mu g\ g^{-1}$ DW)**	**Total chlorophyll ($\mu mol\ g^{-1}$ DW)**
Control	59.4 ab	7.5 a	194 a	13.8 b
Lanthanum	71.9 ab	7.2 a	184 a	12.0 ab
Cerium	103 ab	7.8 a	----*	----*
REE-fertilizer	79.1 ab	7.4 a	211 a	11.9 ab
Calcium	135 a	9.0 a	----*	-----*
Copper	46.3 a	6.4 a	259 a	9.6 a

* No data Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Table 4.26: Influence of REE-fertilizer application rates on mean of α-tocopherol ($\mu g\ g^{-1}$ DW) and total chlorophyll ($\mu mol\ g^{-1}$ DW) in leaf discs of maize and oilseed rape 66 days after sowing (2005)

REE-fertilizer application rates ($\mu g\ g^{-1}$)	Maize		Oilseed rape	
	α-Tocopherol ($\mu g\ g^{-1}$ DW)	**Total chlorophyll ($\mu mol\ g^{-1}$ DW)**	**α-Tocopherol ($\mu g\ g^{-1}$ DW)**	**Total chlorophyll ($\mu mol\ g^{-1}$ DW)**
0	59.4 a	7.5 a	194 a	13.8 a
2.7	86.6 a	7.3 a	184 a	12.2 a
27	64.9 a	7.3 a	189 a	13.6 a
135	73.9 a	6.9 a	233 a	11.3 a
270	95.1 a	8.5 a	248 a	10.2 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

5 Discussion

It was the aim of the present investigations to determine the influence of graded REE applications (La, Ce, REE-fertilizer) on morphological and physiological parameters of maize and oilseed rape and to compare their effects with that of Ca and Cu. La is discussed as a substitute for Ca, and Cu is an essential heavy metal, which enables a direct comparison of effects of different heavy metals. Although nowadays mostly mixtures of REEs are used in fertilizers, it was the aim of this study to distinguish between individual REEs and combined effects. In addition, the effect of graded REE applications on chemical soil characteristics, selected soil microbial enzyme activities (DHA and AlP), and soil microbial counts (heterotrophic bacteria, actinomycetes and fungi) were measured to assess information about the influence of REEs on soil life. The rates of REEs were a manifold of the plant available content of the natural soil and this approach delivers a much better understanding of site-specific effects of REEs when compared to graded applications that have been chosen arbitrarily and which might distort effects.

Rare earth elements (REEs) can be divided into two groups: light and heavy rare earth elements:

(a) Light rare earth elements (LREEs), the light or cerium subgroup, comprising the seven elements (atomic numbers 57- 63) these elements are La, Ce, Pr, Nd, Pm, Sm, and Eu.

(b) Heavy rare earth elements (HREEs), the heavy or yttrium subgroup, comprising the elements with atomic numbers 64-71 as well as Y and Sc, these elements are Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Despite its low atomic weight, yttrium is categorized with the heavy REE (HREEs) because its properties closer to those of the heavier REEs than to the lighter group (Christie et al., 2001). The previous distinction is based on their physical and chemical properties, and ion radius (Hu et al., 2006). On the other hand, Xu et al. (2002) reported that there is a third group called Middle rare earth elements (MREEs) and it comprises Sm, Eu, Gd, Tb, Dy, and Ho.

The discussion comprises the dose/effect relationships of REEs on soil characteristics (chapter 5.1), plant features (chapter 5.2) and an assessment of chances and risks of the use of REEs in agriculture (chapter 5.3).

5.1 Dose/effect relationships of REEs on soil characteristics

The dose/effect relationship describes the relationship between the dose of a substance or factors and its effect on an exposed organism or matter (UN, 1997). Heavy metals belong to the group of trace elements. They comprise Cu, Mn, Fe, Zn, Cr, Cd, Pb, As, Hg, Ni, Co, Tl, and U. For plants, some can be classified as non-essential (like Cr, Cd, Pb, As, and Hg) or essential such as Cu, Mn, and Zn. Non-essential metals may disturb metabolic processes in the plant, even if present in smallest quantities (Renella et al., 2003). They can unfold toxic effects in relation to the dose (Figure 5.1). The use of dose-response curves for quantifying the effects of heavy metals on soil biochemical parameters was proposed by Babich et al. (1983).

Chinese researchers have reported beneficial effects of low doses of REEs on a wide range of crops growing in soils, for example, when applied as foliar sprays, seed treatments, or added to solid or liquid rooting media (Xie et al., 2002). However, these beneficial effects have seldom been reported in other countries. In contrast, REEs were reported to be highly toxic to plants (Hu et al., 2002) and microorganisms (Tang et al., 2004). The harmful effects of excessive REEs on soil microbial biomass (Chu et al., 2001), N transformations (Zhu et al., 2002), CO_2 evolution, and soil enzyme activities (Xu et al., 2004) have been reported in several studies. Until now, however, the application of REEs is not regulated in China, and therefore, there is growing concern about possible adverse effects of an accumulation of REEs in soils (Chu et al., 2007).

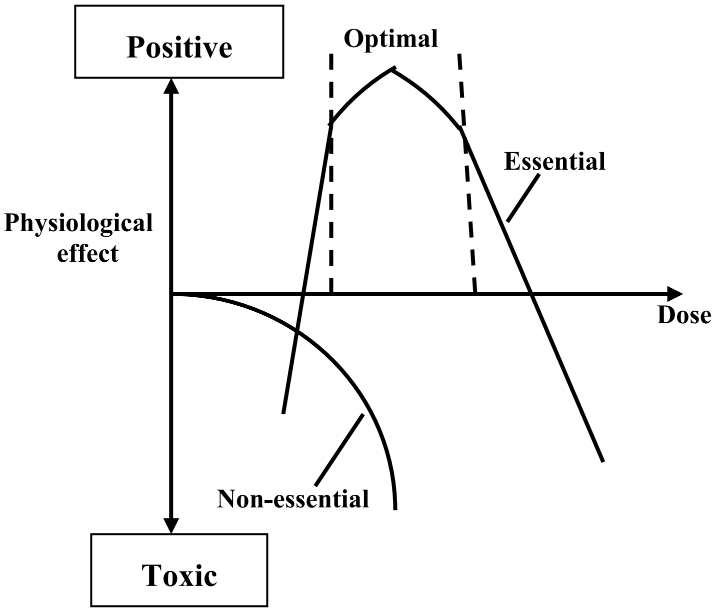


Figure 5.1: Dose-effect relationship of essential and non-essential metals for plant growth (adapted from Bliefert, 1994)

Chemical soil characteristics (soil pH and EC)

Soil pH and redox potential (Eh) are important factors which influence mobility and plant availability of REEs in soils. Cao et al. (2000) studied the effects of pH and Eh on REE desorption in soils. Their results showed that the release of REEs increased with decreasing pH value at constant Eh and it increased when Eh decreased at constant pH values. It seemed that the mobility of La, Gd and Y depended mainly upon pH value, whereas that of Ce was influenced by Eh, too.

In the present study, it was found that REE applications did not significantly influence soil EC in all treatments in 2005. In comparison, in 2006 soil EC values increased by REE applications on non-vegetated soil though this effect was significant only for the Ce and La treatment; on vegetated soil a significant effect was found for Ce applications where maize was grown and REE-fertilizer applications to maize and oilseed rape. It was found also that there was difference between soil EC of vegetated and non-vegetated soil for all treatments. Compared with non-vegetated soil, vegetated soil had a lower salinity; the soil pH values were consistently higher on non-vegetated than vegetated soil in both years. In general, soil EC was higher in case of Ca and Cu in 2005 than of REE applications, but the opposite was achieved in 2006 because of significantly lower Ca application rates used in this experiment. Differences for La, Ce, Ca and REE fertilizer proved to be statistically significant in case of maize and non-vegetated soil in both seasons. The opposite trend was achieved for oilseed rape in 2006. The correlation coefficients (r) for the relationship between soil pH and concentration of REEs in roots and shoots of oilseed rape were negative and not significant in 2005. In general, the soil pH values decreased tendentiously with increasing REE application rates especially in case of non-vegetated soil. These findings are well in accordance with other investigations (Xiong et al., 2000; (Chu et al., 2003).

Chemical conditions in the rhizosphere soils are often different from the bulk soil as plant roots exude organic compounds including low-molecular-weight organic acids (LMWOAs). It is also expected that roots exudate components to regulate their bioavailability and transport in the soil environment. Moreover, root exudation may be an important mediation in altering the species composition of rhizosphere microflora that function in nutrient transformations, decomposition and mineralization of organic substances, and formation of soil organic matter, all of which are related to soil quality (Petra et al., 2004). This latter aspect is particularly in need of clarification, in view of the ever increasing threat of global environmental change and soil pollution caused by anthropogenic activity (Lu et al., 2007).

The soil pH values decreased with increasing REE application rates (Table 4.2). This is may be due to the chelation of REEs by root exudates or plant uptake. It is possible that the reason is an exchange of adsorbed H^+ by REE ions and the liberation of H^+ as a result of the formation of metal-organic chelates. This explains higher pH values in non-vegetated soils, too (Table 4.2).

The soil pH values decreased with increasing REE application rates. This is may due to the chelation of REEs by the exudates of plant roots or plant uptake. It could be thought that the reason due to the exchange of adsorbed H^+ by REE ions and the liberation of H^+ as a result of the formation of metal-organic chelates. This also can be explained the reason of high pH of non-vegetated soil comparing with vegetated soils (maize and oilseed rape).

Chu et al. (2003) studied the effects of soil pH and extractability of La in soils. Two kinds of experiments were carried out (laboratory and greenhouse experiments) to study these effects. The added concentrations of La were as follows: 0, 50, 300, and 1000 µg La g^{-1} dry soil and 0, 30, 150, 300, 600 and 900 µg La g^{-1} dry soil. The authors concluded that application of La decreased soil pH and there were significant negative correlations between soil pH and added La. Significant positive correlations were also observed between 0.05 M HCl extractable La and added La, indicating that exogenous La was highly available in soil. They suggested further that reductions in soil pH are caused by an exchange of adsorbed H^+ by La^{3+}, and the liberation of H^+ is a result of the formation of metal-organic chelates.

Soil microbial enzyme activities (DHA and AlP)

Soil is a complex microhabitat, fundamental and irreplaceable; it governs plant productivity of terrestrial ecosystems and it maintains biogeochemical cycles. The living population inhabiting soil includes macrofauna, mesofauna, microfauna and microflora. Indeed, bacteria and fungi are highly versatile; they can carry out almost all known biological reactions (Nannipieri et al., 2003).

Soil microbial activity is a term used to indicate the vast range of activities carried out by micro-organisms in soil, whereby biological activity reflects not only microbial activities, but also the activities of other organisms in the soil, including plant roots (Nannipieri et al., 1990). Various methods have been used to determine microbiological activity.

Stable extracellular enzyme activities are associated with soil colloids and persist even in harsh environments that would limit intracellular microbiological activity (Nannipieri et al., 2002). Thus, only strictly intracellular enzyme activities can truly reflect microbial activity because the contribution of free extracellular enzyme released by active soil microbial cells is negligible; indeed, these enzymes are short-lived because they are degraded by proteases unless they are adsorbed by clays or immobilized by humic molecules (Burns, 1982). Unfortunately, the enzyme assays used in the present investigation do not distinguish the contribution of intracellular from extracellular and stabilized soil enzyme activities, which seems to be, however, an acceptable shortcoming as it was the main target to determine the main effects of graded REE applications.

Investigations on a limited number of enzymes show that agricultural management practices affect their activities (Dick, 1994). Soil enzyme assays provide quantitative information on soil chemical processes, nutrient mineralization rates, and organic matter accumulation. Soil enzyme assays among different management practices may also indicate short-term differences in soil quality improvement, and can be used to evaluate rapid responses to changes in management and in understanding sensitivity to environmental stresses (Dick, 1997). Research shows that fluorescein diacetate (FDA) hydrolysis, β-glucosidase, glucosaminidase, and dehydrogenase activities are good indicators of soil biogeochemical processes (Udawatta et al., 2008). This was one of the reasons why the dehydrogenase activity was determined in this investigation.

Among the different enzymes in soils, dehydrogenase, β-glucosidase, urease and phosphatases are important in the transformation of different plant nutrients. Dehydrogenase activity (DHA) reflects the total oxidative activity of the microbial biomass (Nannipieri et al., 1990) and does not function extracellularly (Tripathi et al., 2007). Acid phosphatase is released by roots and soil microorganisms, whereas alkaline phosphatase (AlP) is only produced by microorganisms. Acid and alkaline phosphatase activities are often increased in the rhizosphere compared to the bulk soil (Tarafdar and Claassen, 1988).

Many studies related to the toxicity of metals on enzyme activities in soils are available in the literature (Stuczynski et al., 2003), but data on the effect of REEs is limited and thus deliver an important contribution to soil environmental aspects of the use of REEs.

In this present work, in general, with increasing rates of REEs DHA and AlP activities decreased. Results showed that there was no significant effect of REE-fertilizer applications on AlP in non-vegetated soil in both seasons, whereas Cu, La and Ce applications affected significantly the AlP activity. Ce application rates significantly reduced/increased AlP when maize and oilseed rape was grown in 2006. La and Ca application rates did not significantly affect AlP activity in vegetated soils. The AlP values were higher on vegetated soil compared with non-vegetated soil. These results are in accordance with the results of Tarafdar and Claassen (1988), who found an increased AlP activity in the rhizosphere compared to the bulk soil.

The relationships between soil pH, EC and soil microbiological parameters (DHA, AlP and soil microbial counts), mineral composition of roots and shoots and uptake of REEs and essential nutrient by maize and oilseed rape were tested. Graded REEs application rates resulted in a lower soil pH value and decreased soil enzyme activities.

It is well documented that some heavy metals such as copper, although essential for plant growth, are toxic to plants at high concentrations. There is also increasing evidence that some soil microorganisms are more sensitive to heavy metal stress than plants. As copper is usually strongly adsorbed onto the soil constituents, especially to organic matter, clays and oxides, Cu-accumulation is likely to remain in most soils for a long time. Thus Cu-accumulation has potentially a long-term impact on a large range of soil biota. Several studies have shown that high concentrations of heavy metals decrease the microbial biomass and functional diversity of soil micro-organisms, and thus the biological activity of soils (Khan et al., 2000).

Toxic effects of heavy metals on enzyme activity have been studied in soil by calculating the ecological dose (ED_{50}) value (Haanstra et al., 1985; Moreno et al., 2001). The alkaline phosphatase was more sensitive in the acid and neutral soil whereas the acid phosphatase was more sensitive in the alkaline soil. Both phosphatase activities and the ATP content were more sensitive in the sandy than in the finer textured soils (Renella et al., 2003). The results of the present work had the same trend where, the AlP and DHA values decreased with increasing Cu application rates (Table 4.8).

Several approaches have been used to estimate the microbial biomass in soil. The dehydrogenase activity (DHA) is the most widely used enzyme indicator of soil biological activity and for estimating the microbial biomass (Vogeler et al., 2008). Results of Vogeler et al. (2008) showed that plants (*Agrostis capillaris*) increased the DHA in the low Cu soil (2.4 $\mu g\ g^{-1}$). These results agree with findings of the present work, where the DHA values were higher in presence of plants than of absent (Table 4.8).

Soil microbial counts (heterotrophic bacteria, actinomycetes and fungi)

Plants can affect the soil biota by influencing the quantity and quality of organic substrates that are released (Viketoft et al., 2005). It is well known that different plant species can associate with microbial communities with unique characteristics (Chen et al., 2002; Viketoft et al., 2005) probably due to differences in amount and quality of root exudates (Nguyen, 2003). Coexistence of multiple plant species may enhance the complexity of soil microorganisms by increasing the heterogeneity of organic substrates during decomposition of litter and living roots (Broughton and Gross, 2000; Stephan et al., 2000). Furthermore, plants may also play important roles in determining soil enzymes activities, as extracellular enzymes are derived mainly from soil microorganisms, plant roots and soil animals (Yang et al., 2007).

Biosorption of heavy metals by microbial cells has been recognized as a potential alternative to existing technologies for removal of these contaminants from polluted soils and waters. This phenomenon is generally described as retention of ions from solution by microbial cells and this metal uptake is normally very efficient and frequently selective (Ledin, 2000; Ozer et al., 1999). Characteristics of the biosorption process can also be exploited for concentration and selective recovery of more valuable metals. The uptake of metal ions by microorganisms has been shown to occur in two ways: passive and/or active. During the passive uptake (biosorption), the metal ions are quickly adsorbed onto the cell surface of the biomass during its contact with the metal solution (physical adsorption or ion exchange at the cell surface). The active uptake (bioaccumulation) is a slower process involving the transport of ions across the cell membrane toward the cytoplasm occurring only in living cells (Donmez et al., 1999). Dead cells have been preferred over living biomass in biosorption processes due to non-limiting conditions imposed by cellular growth (Palmieri et al. 2002).

Many reports showed that soil microorganisms and material transformations are influenced by heavy metals (Hu et al., 1990), and some reports also showed that microbial activities are affected by REEs (Chu et al., 2002b). La had a stimulative effect on the nitrification and P transformation in red soil when the concentration of La is below 100 and 300 µg g^{-1}, respectively, but the higher concentration has inhibitory effect and the inhibition is strengthened with increasing concentration of La (Chu et al., 2002b). La inhibited strongly the phenol decomposition in red soil and the inhibition was strengthened with increasing concentrations of La (Chu et al., 2002a).

Nevertheless studies were performed to reveal to which extent REEs may influence the soil system. Although REEs have been shown to affect soil nitrification, effects were smaller than those of heavy metals. Inhibition only occurred at high concentrations, whereas 5 µg g^{-1} were considered as the non observed effect level (NOEL). With view to currently applied doses of REEs in Chinese agriculture, no inhibitory effects on soil nitrification and ammonification are expected from long-term application (Liu and Wang, 2001).

At high concentrations, REEs have been shown to change the ecological structure of microorganisms in soil with inhibitory effects occurring in the following order: bacteria > actinomycetes > fungi (Tang et al., 2004). In addition, stimulation of fungi was reported at high REE concentrations (Xiong and Zhang, 1997). Therefore, a critical limit of a soil content of 30 µg g^{-1} was determined REEs (Redling, 2006).

At high concentrations of 10^{-4} - 10^{-2} mol L^{-1}, REEs have been shown to inhibit bacterial growth, whereas growth stimulating effects occurred at low concentrations of about 10^{-5} mol L^{-1}. For Ce, concentrations ranging from 10^{-3} mol L^{-1} to 10^{-2} mol L^{-1} inhibited the growth of several bacteria including *Escherichia coli*, *Bacillus pyocyaneus*, *Staphyloccous aureus*, *Leuconostoc* and *Streptococcus faecalis* (Zhang et al., 2000b). After entering the soil, heavy metal elements usually stimulate soil bacteria at low level while harming them at high level. Similarly, REEs may change the population of microorganism found in the soil system to various extents (Tang et al., 2004). It was reported that various microorganisms present a high capacity of absorbing REE ions, such as Gd^{3+} (Andrès et al., 2000).

At moderate concentrations, La increased the soil microbial biomass as well as the population of bacteria, actinomycetes, azotobacter and nitrifying bacteria, whereas excessive applications resulted in the inhibition of all microbial properties of the soil (Chu et al., 2001b; Chu et al., 2001a). Inhibitory effects in association with increasing doses were also observed by Xu and Wang (2001), while stimulating effects of La on microbial biomass were not found. Non observed effect concentration (NOEC) was reported to be 432 µg La per g soil (Xu and Wang, 2001). Consistent with Xu and Wang (2001), Chang (2006) observed inhibitory effects on the total number of soil bacteria after REEs accumulated at 5 to 50% of absorption capacity (ADC).

A recently conducted study on the ecological effects of low dosage mixed REE accumulation on major soil microbial groups' revealed continuous stimulation of soil fungi and alternative effects of stimulation, inhibition and re-stimulation on soil bacteria and actinomycetes (Tang et al., 2004). Inhibitory effects of REEs on the three groups of soil microorganisms were in the order of bacteria > actinomycetes > fungi. A remarkable change in the population structure of these soil microorganisms were observed at an accumulation rate of 150 µg g^{-1} of REEs (Ma et al., 1996). But median effect concentrations (EC_{50}) of REEs were 24.1 µg g^{-1} for soil bacteria, 41.6 to 73.8 µg g^{-1} for actinomycetes and 55.3 to 150 µg g^{-1} for fungi (Ma et al., 1996). In contrast, no obvious influence of REEs on soil bacteria was observed by Ma et al. (1996), whereas the biomass of soil fungi and actinomycetes increased by a factor of ten and two to three, respectively. Stimulation of fungi and actinomycetes at high levels of La was also observed by Xiong and Zhang (1997), while low accumulation levels inhibited bacteria (Redling, 2006).

In the present study, the microbial counts in relation to the REE dose decreased in the order heterotrophic bacteria > actinomycetes > fungi. For the present study, the results were in a good agreement with the results found in literature mentioned above. For heterotrophic bacteria, the biggest number (7.1×10^7 and 4.0×10^7) was obtained at a level of 50 µg La g^{-1} in case of maize in 2005 and 2006, respectively. In comparison, the microbial counts were 3.5×10^6 and 2.5×10^6 and 1.1×10^6 and 2.8×10^6 in case of actinomycetes and fungi in 2005 and 2006, when maize was grown at a level of 100 and 50 µg La g^{-1} and control, respectively.

REEs have stimulative effects on microbial functions (biomass and respiratory rate), when concentrations are lower than 100 µg g^{-1} (Zhou et al., 2004). Inhibition effects can be expected when concentrations were higher than 500 µg g^{-1} in a paddy soil in China (Zhou et al., 2004). In pot culture experiment, Chu et al. (2001a) investigated the influence of graded La application rates (from 0 to 900 µg g^{-1}) on soil microbial counts. They found that addition of La into the soil at the level below or equal to 300 µg g^{-1} increased the number of bacteria; however the bacteria counts decreased at the level over 300 µg g^{-1}. For actinomycetes, the number slightly increased up to a dose of 150 µg g^{-1}. Fungi counts at all levels of La decreased with graded La application (Chu et al., 2001a). These indicated that La had stimulative effect on soil bacteria and actinomycetes at low levels and an inhibitory effect on soil bacteria, actinomycetes and fungi at high levels (Chu et al., 2001a).

The soil microbial community was significantly affected by Cu additions when oilseed rape was grown; in presence of maize the number of fungi was reduced, however not significantly (Table 4.4). Soil microbial communities decreased by increasing of Cu application rates for both crops. Only the number of actinomycetes increased up to a Cu rate of 43 µg g^{-1} when maize was grown (Table 4.4).

Differences in the microbial activities (DHA and AlP) and microbial communities' composition between rhizosphere of maize and oilseed rape, and non-vegetated soil with different Cu concentrations were distinct (Table 4.8). In case of vegetated soil, the soil microbial activities (DHA and AlP) were higher than that of non-vegetated soil. Soil microbial counts of oilseed rape were higher than that of maize, where the microbial counts were 3.3×10^7, 2.3×10^6, and 5.5×10^5 for heterotrophic bacteria, actinomycetes and fungi, respectively. The microbial counts values of maize were 2.9×10^7, 2.3×10^6, and 4.9×10^5 for heterotrophic bacteria, actinomycetes and fungi, respectively (Table 4.4).

In the present study, the application of REE fertilizer decreased the number of fungi in pots grown with oilseed rape, while no similar effect was observed for maize (Table 4.4). Interestingly, Cu reduced all three microbial parameters irrespective of the crop. In general, La, Ce and REE-fertilizer applications resulted in a higher number of microbial counts, whereby this effect was more pronounced for maize. Also Ca rates equivalent to that of La and Ce yielded a significant increase in the number of heterotrophic bacteria and actinomycetes in maize pots (Table 4.4). It is known that Ca is an essential nutritional element for plants. Regarding their chemical properties, a lot of physiological effects of REEs were attributed to the resemblance of individual REEs, especially La, to Ca.

The relations between soil pH, EC and microbiological parameters were tested for maize and oilseed rape. The results presented in Table 4.5 and 4.6 reveal that highly negative, significant correlation coefficients (r) were found between fungi and soil EC and pH. The correlation coefficients (r) values r= - 0.57**, r= - 0.73** and r= - 0.90, r= 0.37** for maize and oilseed rape, respectively (Figure 4.2).

5.2 Dose/effect relationships of REEs on plant characteristics

The uptake of metallic elements by plant cells, especially in the roots, is facilitated by transport mechanisms, since several heavy metals are in fact required by plants as micro-nutrients. The plant can not, however, prevent toxic elements from entering by the same mechanisms. The toxicity of heavy metal ions is chiefly due to their influence with electron transport in respiration and photosynthesis, the inactivation of vital enzymes (like for instance: ATPase, phosphatase, malate dehydrogenase etc) (Larcher, 2003).

According to plant metal uptake, it could be classified plants into following four groups:

(1) Excluders: plant with restricted uptake of toxic metals or restricted translocation into the shoot over a wide range of soil metal concentrations

(2) Index plants: plants those uptake and translocation reflect soil metal concentrations

(3) Accumulators: plant which actively concentrate metals in their tissues

(4) Hyper-accumulators: plants in which the tissue metal concentration can exceed 1000 µg metal g^{-1} (Ross, 1994).

Fractionations of REEs and their mechanisms in soybean were studied through application of exogenous mixed REEs under hydroponic conditions (stock solution of 2.1 mmol L^{-1} mixed REEs) (Ding et al., 2007). Significant enrichment of middle REEs (MREEs) and heavy REEs (HREEs) was observed in plant roots and leaves respectively, with slight fractionation between light REEs (LREEs) and HREEs in stems (Ding et al., 2007). REE fractionations are supposedly dominated by fixation mechanism in roots caused by cell wall absorption and phosphate precipitation, and by combined effects of fixation mechanism and transport mechanisms in aboveground parts caused by solution complexation by intrinsic organic ligands (Figure 5.2, Ding et al., 2007).

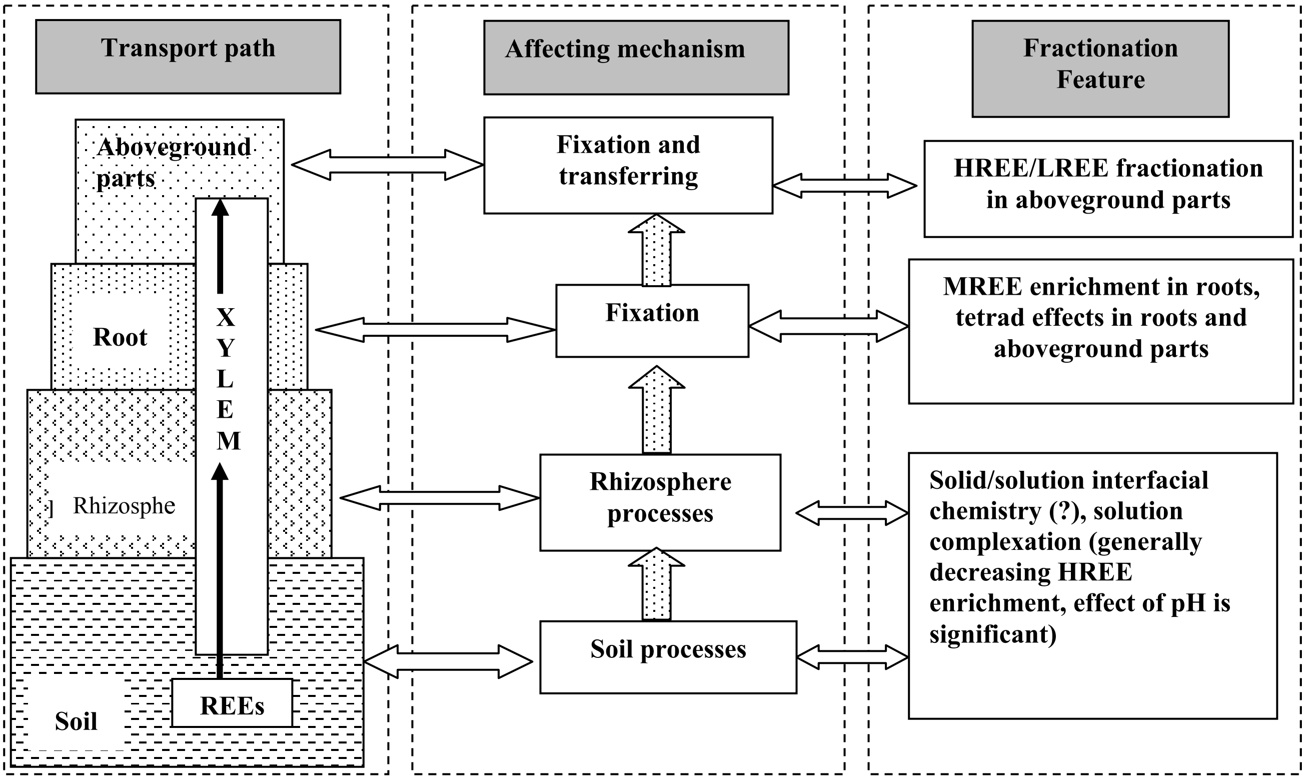


Figure 5.2: Conceptive model of REE fractionations in plants (adapted from Ding et al., 2007)

Plant growth and germination rate

The results from the few existing studies on the effect of REEs on plant growth are contradictory. Early reports indicated that REEs had an inhibitory effect on plant growth (Wheeler and Power, 1995). For example, La^{3+} and Nd^{3+} were found to inhibit the elongation of oat coleoptile sections (Pickard, 1970). Colloidal La caused an almost complete inhibition of cell division and root elongation in the root tips of barley plants (van Steveninck et al., 1976). Diatloff et al. (1995) also reported that root length of maize and mung bean decreased with increasing concentration of La and Ce. In a solution culture with wheat, the estimated toxicity threshold of La^{3+} in shoots was 0.09 mg g^{-1} of dry matter and 3.0 mg g^{-1} of dry matter in roots. Plant toxicity in relation to different elemental applications expressed as a reduction in yield by 50% increased in the order Mn < Zn < Fe < La < Cu in shoots and Mn < Zn < Fe=La < Cu < B in roots (Wheeler and Power, 1995).

Common responses of plants in terms of yield to REE applications are to be in the order of 5 to 15% and sometimes even higher (Xiong, 1995). In addition to plant yield increases, improvements in product quality, comprising increased sugar content in sugar cane, increased vitamin C content in grapes and apples and increased fat and protein content in soybean (Brown et al., 1990); (Wan et al., 1998) have also been reported for a wide range of crops. Growth promotion after REE application was also observed in potatoes in pot experiments (Jie, 1987). In contrast, REE supplementation was reported to decrease the content of chemical residues in several crops such as rice, orange, water melon, grape and pepper (Redling, 2006). In previous studies it has been shown that the upper threshold of REE concentration which yield detrimental effects varies between crop species (Redling, 2006). Generally, except for oilseed rape, growth promotion was found by the application of less than 1 g kg^{-1} REE oxides to the soil, while the use of more than 1-2 g kg^{-1} REE oxides caused inhibitory effects (Chang et al., 1998).

For the present results, the influence of REE applications on plant biomass, germination rate and plant height of maize and oilseed rape was investigated. In general, REE applications decreased germination rate and plant height for each crop and both seasons in a dose-dependent way. The highest plant biomass production was obtained at 24.9 and 31.5 g pot^{-1} for maize when 2.7 µg g^{-1} REE-fertilizer was applied; in case of oilseed rape 2.7 and 27 µg g^{-1} REE-fertilizer rates caused the highest yield with 20.9 and 13.8 g pot^{-1} in 2005 and 2006, respectively. This means with increasing graded REE-fertilizer application rates (up to 270 µg g^{-1}), the plant biomass production decreased and the highest values were obtained at low levels (2.7 or 27 µg g^{-1}) for maize and oilseed rape, respectively. The lowest plant biomass production was consistently found at the highest application rate 270 µg g^{-1}. Obviously only low levels of REEs stimulated plant growth while higher rates led to yield decreases.

In 2005, all plants died off when the third and fourth-fold plant available content of Ca and Cu was applied due to salt and heavy metal stress. In 2006, the results clearly reveal that only the application of REE fertilizer yielded a significant decrease of the germination rate of maize, while plant height was reduced in oilseed rape, too. These effects were significant when the highest REE rate of 270 µg g^{-1} was applied. In 2006, maize correlated significantly via germination rate and plant height with plant biomass (root dry matter, shoot dry matter and total biomass). The (r) values were 0.06, 0.82**, 0.84** for plant height and 0.41**, 0.49**, 0.49** for germination rate for roots, shoots and total biomass, respectively.

Essential nutrients and beneficial elements are often toxic to plants when supplied at excessive concentrations. The identification of threshold concentrations for the toxicity of La and Ce to plants provides an indication of the concentration which may not be exceeded by any means. Change in root length provides a rapid and sensitive indicator of toxicity. Toxicity to plants of aluminium (Al), a trivalent ion similar to La and Ce can be alleviated through complexation by humic acid (HA) and fulvic acid (FA) that are present in soil solution (Harper et al., 1995). There is evidence that REEs also form strong complexes with HA and FA (Bidoglio et al., 1991), but it is not known whether such complexes can overcome the phytotoxic effects of La. Consequently, the effects of varying La or Al concentrations (0 to 30 µM) on maize root elongation were examined in the presence and absence of HA and FA (Diatloff et al., 1995).

Concentration and uptake of REEs and essential nutrients

Mineral elements are transported over a long distance in plants within two tissues, xylem where water and minerals are transported from roots to shoots and phloem where assimilates and metabolites are transported from mature leaves (source) to areas of growth and storage e.g., seeds (sink), roots.

Concentrations for REEs in plants reported in the literature vary several orders of magnitude. Therefore, it is difficult to communicate any “typical” concentrations of REEs in organs of vascular plants (Tyler, 2004). In general, a higher availability of REEs in the soil causes a higher REE uptake by plants (Liang et al., 2000). The uptake of La and Ce is very fast, but their transport from roots to shoots is much slower, so that La and Ce are accumulated in roots. Roots are an efficient barrier for the translocation of heavy metals to shoots (Zhang et al., 1999). The results of the present investigation confirm this basic finding.

Roots of maize and mung bean grown in solution culture accumulated 20 – 150 times higher La concentrations than their shoots (Diatloff et al., 1995) and similar root/shoot ratios were measured in *Agrostis capillaries* grown in soil cultures.

The distribution patterns of REEs in native plants have been widely studied. The REE content usually decreased in the order root > leaf > stem > flower, grain, fruit. Similar results were reported for maize and rice. However, slight variations in the distribution pattern have been observed among individual REEs. Light REE concentration decrease in the order lamina > root > stem > petiole, while heavy REE contents decrease in the order root > lamina > stem > petiole or even root > stem > lamina > petiole (Redling, 2006).

Using both pot and plot experiments, the dose-dependent accumulation of REEs in maize (*Zea mays* L.) after application of an REEs mixture (1, 5, 10, and 20 µg REEs g^{-1} and 16, 32, and 64 mg REEs m^{-2}, for pot and plot experiments, respectively) was measured (Wang et al., 2001c). In the pot experiment, the dose-dependent accumulation of REEs in maize root and stem was observed, but it could not be detected in maize leaf under the dosage of 20 µg REEs g^{-1} soil. The non-observed effect concentration (NOEC) for accumulation of REEs in maize seedling with the pot experiment was 1.0 µg REEs g^{-1}. In the plot experiment, the dose-dependent accumulation was observed at an early stage after application of REEs and the NOEC value of 32 mg REEs m^{-2} was obtained. At harvest (57 days from application), no dose-dependent accumulation of REEs was observed in any part of the maize. They observed that the plant shows no preference on individual REE and the results of fingerprinting indicated clearly the incorporation of exogenous REEs in plant tissues, in a similar manner as that observed in the dose-dependent distribution of REE concentrations. These results indicated also a translocation process of REEs from plant root to leaf when applied to soil or from leaf to root when applied to leaf. A homeostatic regulation mechanism for excessive uptake of REEs in plants is suggested to regulate the concentrations of REEs in the plant.

In the present study, the REE content of roots and shoots increased with increasing REE application (La, Ce and REE-fertilizer). In both crops the highest concentration of REEs was in roots when compared to shoots. Oilseed rape contained on average 2.2 and 2.0 times higher REE concentrations in roots and shoots than maize, respectively (see chapter 4.3.2, Table 4.18a). It was found that uptake of REEs in different parts of plants decreased in the following order: root > shoots and that of individual REEs in the control treatments in the order: Ce > La > Nd >Pr in both plant parts and in each crop. With increasing application rates of La, Ce and REE-fertilizer the concentration and uptake of La, Ce and REEs (La, Ce, Pr and Nd) increased significantly in roots and shoots of both crops. These results are in agreement with previous investigations (see above).

The relationship between chemical soil characteristics (EC and pH) and concentration of REEs in roots and shoots of maize and oilseed rape in 2006 was highly positive and significant for both crops (see chapter 4.3.2).

The application of La influenced the mineral composition of mung bean and maize (von Tucher et al., 2001). The N, P, Ca, Mg, S, Mn content was significantly higher in leaves of mung bean, while the K content decreased by up to 60% (von Tucher et al., 2001). In maize, a significantly higher content was observed for Ca, Mg in shoots and Mn in roots (von Tucher et al., 2001). In addition, Mn deficiency was expressed in mung bean plants treated with a solution containing more than 0.09 µg L^{-1} of Ce (Diatloff et al., 1995d). Velasco et al. (1979) suggested that REEs might reduce B uptake and thus cause B deficiency. In comparison, increased uptake of Zn, Mn and Mo was observed in maize plants after rare earths were applied at 5 mg L^{-1}, while at 10 mg L^{-1} (Chang, 2006).

Despite the effects of La on Ca depending processes (Redling, 2006) as well as on several cellular functions, REEs have no known biological function in this field. However, even though there is no evidence available at present, it might even be possible that REEs are essential trace elements for humans and animals. This has been hypothesized as REEs occur ubiquitously in soils and plants (Wyttenbach et al., 1998b; Krafka, 1999), commercial feed and in tissues of humans and animals (Evans, 1990; (Eisele, 2003; Borger, 2003; Kraatz et al., 2004; Redling, 2006).

Brown et al. (1990), who reviewed the effects of REEs on physiological functions of Ca in plants, reported that REEs acted analogous to Ca. La was shown to inhibit many enzymes as well as functional proteins (Brown et al., 1990). La was able to displace Ca from extra-cellular binding sites thereby inhibiting the efflux of extra-cellular and partly intracellular Ca (Brown et al., 1990). Similar to Ca, La could restrict K uptake in plants if applied for a short time, however long-time application resulted in accelerated K uptake (Leonard et al., 1975). Nevertheless, the interference of REEs, especially of La, with several Ca functions probably accounts for many effects observed in plants, including toxic effects (Pang et al., 2002). Besides influencing physiological processes involving Ca, REEs may also affect the Ca metabolism itself (Redling, 2006). Diatloff et al., (1995c) found that Ca concentration decreased by 41% in maize roots that were treated with a solution of 0.2 µg La L^{-1}. Another study showed that Gd and La inhibited Ca uptake by plant protoplasts even to a higher extent than Al. Yet in contrast to Ce, which showed the same pattern of inhibition of Ca uptake, Ca uptake was totally unaffected by Sc (Rengel, 1994b). In accordance with Hodick and Sievers (1988), inhibitory effects of La were attributed to the introduction of positive charges into the area of Ca^{+2}-ATPase, thus altering the net charge of cell membranes (Ogurusu et al., 1991). Rengel (1994a) showed that La could inhibit Ca channels and thereby the uptake of Ca.

Paradoxically, it has been reported that the addition of La and also Ce can diminish symptoms in plants caused by Ca deficiency (Weng et al., 1990). Lacking Ca usually leads to the destruction of plant cells due to malfunctioning of the cytoplasm membrane (Xing et al., 1989) (Redling, 2006). Dong et al. (1993) demonstrated that La chloride accelerated growth and root activity and furthermore improved the activity of K^{+} and Mg^{+2}-ATPase in the cytoplasm membrane of cucumber under conditions of Ca deficiency. In soil culture experiments, it was shown that La (> 100 µg g^{-1}) increased the Ca content in the sap of rice (Chang, 2006). Increased Ca contents were also observed in the cell wall of tobacco callus and oilseed rape seedling root after La or Ce were applied at low concentrations (1.4 - 6.9 mg L^{-1}), whereas higher concentrations (13.9 mg L^{-1}) caused a decrease (Redling, 2006).

Figures 4.9 and 4.10 of the present work show the relationship between Ca concentrations in roots and shoots of maize and REEs (La, Ce, Pr and Nd). The relationship between Ca concentration in maize roots and LREE concentrations in maize roots proved to be negative, but not significant. In comparison, the relationship was positive and highly significant in maize shoots. The relationship between REE and Ca uptake was negative and significant for both roots and shoots of maize.

In case of oilseed rape, the relationship between Ca and La/Ce/Pr/Nd concentration/uptake was negative and non-significant for both roots and shoots. These results are in agreement with that of other researchers e.g. Diatloff et al., (1995c); Hodick and Sievers, (1988); Rengel (1994a); Rengel (1994b). It should be noticed that the correlation between REE concentrations in plant parts (roots and shoots) was linear for both crops. This means that the ability of these plants to take up REEs has not been fully exploited in the current investigation.

Soil/plant transfer of REEs

Transfer ratios of REEs from roots to leaves were higher for LREEs than HREEs (Tagami and Uchida, 2006). The reason was probably that the nutrient solution contact time in their study was only short. They assumed that REEs when bound to proteins on root surfaces pass fairly slowly through the root surface to the xylem and that this process depends on their ionic radius. The high concentration ratio of LREEs supports this hypothesis.

The soil-to-plant transfer factor (TF) is broadly used as one of the parameters to estimate the intake of radionuclides through food ingestion. The TF values vary within several orders of magnitude (Uchida et al., 1987). The variation of TF values reported in literature may be a result of many factors such as soil pH, soil type, physicochemical form of elements in soil, oxidation-reduction potential (Eh) in soil, experimental methods (field, lysimeter and pot), kinds of plants, treatment of plants (wash, peel, etc.) and others (Uchida et al., 1987).

In a study of Ban-Nai et al. (1999) the soil-to-plant transfer factors (TFs) of some selected radionuclides (Cs, Sr, Co, Mn, Zn and Ce) were obtained for edible parts of root vegetables grown on an Andosol (as a representative of Japanese soils). The TF for ^{141}Ce from the soil to the edible part of carrots was 0.0002. The transfer factor for edible parts of root vegetables was for all elements lower than those for leaf parts.

In order to obtain soil-to-plant transfer factors (TFs) of radionuclides under equilibrium conditions, naturally existing elements were measured as analogues of radionuclides. Uchida et al. (2007a) collected 62 plant samples from upland fields throughout Japan and 40 elements including REEs were used to calculate their TFs. The TF-GMs (transfer factor as a geometric mean) of essential elements for plants were usually higher than non-essential elements, such as U, Th and REEs. The mean TFs for REEs varied between

0.0004 and 0.035 (Table 5.1). Table 5.1 shows a comparison between TF-GMs of REEs and TF-GMs of Mn, Co, Zn, Sr, and Cs of some crops collected from Japan and the present results.

Table 5.1: Transfer factors (TF-GMs) for non-REEs (Mn, Co, Zn, Sr, and Cs) comparing with TF of REEs (La, Ce, Pr, Nd, and Sm) for some crops collected in Japan and the present work (dry weight basis)

Crop	**Non-Rare earth elements**					**Reference**
	Mn	**Co**	**Zn**	**Sr**	**Cs**	
Cabbage	1.4E+00	8.1E-02	6.9E-01	8.1E-01	8.1E-01	Ban-Nai et al. (1995)[a)c)]
	2.5E-02	7.0E-03	1.9E-01	2.3E-01	6.7E-03	Tsukada and Nakamura (1998) [b)c)]
	2.8E-02	4.3E-03	2.8E-01	5.3E-01	8.8E-03	Tsukada and Nakamura (2002) [b)]
	2.9E-02	6.0E-03	2.0E-01	1.7E-01	3.3E-03	Uchida et al. (2007a) [b)]
Chinese cabbage	1.7E+00	1.1E-01	2.1E+00	9.4E-01	9.4E-01	Ban-Nai et al. (1995)[a)c)]
	3.7E-02	6.5E-03	9.1E-01	4.2E-1	3.0E-02	Tsukada and Nakamura (1998) [b)c)]
	1.2E-02	3.3E-03	2.8E-01	5.0E-01	5.9E-03	Uchida et al. (2007a) [b)]
Japanese radish	4.0E-01	8.0E-02	8.0E-01	1.0E+00	4.0E-01	Ban-Nai et al. (1999)[a)c)]
	1.2E-02	6.2E-03	8.4E-01	1.6E-01	9.8E-03	Tsukada and Nakamura (1998) [b)c)]
	1.0E-02	4.6E-03	1.5E-01	1.5E-01	2.8E-03	Uchida et al. (2007a) [b)]
Carrot	1.5E+00	3.3E-02	1.4E+00	8.0E-01	9.3E-02	Ban-Nai et al. (1999)[a)c)]
	1.8E-02	2.4E-03	5.3E-01	9.6E-02	1.1E-02	Tsukada and Nakamura (1998) [b)c)]
	6.0E-03	1.3E-03	1.1E-01	8.2E-02	4.7E-03	Uchida et al. (2007a) [b)]
Brown rice	4.6E-02	9.3E-04	2.4E-01	3.1E-03	9.5E-04	Uchida et al. (2007b) [b)]
White rice	1.6E-02	4.6E-04	2.0E-01	8.6E-04	5.9E-04	Uchida et al. (2007b) [b)]
	Rare earth elements					
	La	**Ce**	**Pr**	**Nd**	**Eu**	
Cabbage	1.0E-03	5.0E-04	4.3E-04	4.4E-04	n.d	Uchida et al. (2007a) [b)]
Chinese cabbage	3.8E-03	1.4E-03	1.8E-03	1.6E-03	1.2E-03	Uchida et al. (2007a) [b)]
Japanese radish	2.0E-03	1.5E-03	1.5E-03	1.5E-03	1.9E-03	Uchida et al. (2007a) [b)]
Carrot (leaves)	3.5E-02	2.6E-02	2.8E-02	2.7E-02	2.4E-02	Uchida et al. (2007a) [b)]
Brown rice	4.9E-05	3.3E-05	6.4E-05	5.0E-05	2.6E-04	Uchida et al. (2007b) [b)]
White rice	3.5E-05	3.3E-05	1.1E-04	3.0E-05	3.1E-04	Uchida et al. (2007b) [b)]
Soybean (roots)	1.6E-01	1.5E-01	1.4E-01	1.3E-01	1.1E-01	Nakamaru et al. (2006)[d)]
(stems)	4.4E-03	8.4E-04	6.0E-04	7.0E-04	5.5E-04	
(seeds)	1.9E-04	4.3E-04	2.5E-04	1.3E-04	5.5E-04	
(pods)	4.3E-04	2.1E-04	1.2E-04	1.7E-04	3.5E-04	
Soybean (roots)	6.4E-02	5.3E-02	5.2E-02	5.2E-02	3.5E-02	Nakamaru et al. (2006)[e)]
(leaves)	5.7E-03	4.7E-03	3.4E-03	3.2E-03	3.3E-03	
(stems)	1.3E-03	9.4E-04	9.4E-04	8.7E-04	1.5E-03	
(seeds)	7.3E-04	1.6E-03	5.9E-04	5.3E-04	9.0E-04	
(pods)	5.5E-04	3.4E-04	3.5E-04	3.1E-04	1.1E-03	
Maize (roots)	4.2E+00	11E+00	4.5E+00	4.7E+00	n.d	Present results
(shoots)	9.1E-02	2.8E-01	n.d	8.4E-02	n.d	
Oilseed rape						
(roots)	9.3E+00	23E+00	9.3E+00	9.5E+00	n.d	Present results
(shoots)	1.8E-01	3.7E-01	5.1E-01	1.4E-01	n.d	

[a)]radiotracer experiment, [b)]field observation, [c)]data (dry) were calculated using dry/fresh ratio from TF (fresh) values, [d)]pot experiment at mature stage (84 days from cultivation), [e)]pot experiment at podding stage (61 days from cultivation), Present results were from the control, n.d: not determined.

TF-GMs, transfer factor as a geometric mean and only values in case of Nakamaru et al. (2006) are means.

In the present study, in general, for the individual REEs the TF values decreased in the order Ce > La > Nd > Pr when graded REE-fertilizer was applied in case of roots of maize and oilseed rape, whereas TF values decreased in the order Ce > La > Pr > Nd in the control pots of roots of maize and shoots of both maize and oilseed rape (see Tables 4.23a and b). The TF values of the control pots of oilseed rape shoots were in order of Pr > Ce > La > Nd. The highest TF values were determined for individual REEs when REE-fertilizers were applied; the TF values proved to be higher than for the application of La, Ce and Ca in case of roots of both maize and oilseed rape. The results had not clear trend in case of shoots of maize and oilseed rape. It could be noticed that with REE-fertilizer application rates increasing, the TFs decreased for REEs (La, Ce, Pr, and Nd) decreased up to 135 $\mu g\ g^{-1}$ in case of roots and shoots of maize, whereas up to 270 $\mu g\ g^{-1}$ in case of roots and shoots of oilseed rape.

Stress-related enzyme activities of plants

Both abiotic and biotic stress induces the synthesis of reactive oxygen species (ROS) in plants that can cause damage to the tissues and/or triggers physiological defense responses (Dat et al., 2000). Kubo et al. (1999) found that the response of antioxidant enzymes in *Arabidopsis thaliana* differ with the environmental stress imposed (Davis and Swanson, 2001).

Abiotic stress conditions cause extensive losses to agricultural production worldwide. Stress conditions such as drought, salinity or heat have been the subject of intense research (Bray et al., 2000). However, in the field, crops and other plants are routinely subjected to a combination of different abiotic stress factors (Moffat, 2002). And various abiotic and biotic stress factors may multiply plant response, or show yet unknown interactions. Assuming corresponding interactions for REEs this stresses the significance of environmental conditions on the results obtained. In the worst case this may even mask the direct effects of the treatment.

In the present investigations tocopherol and chlorophyll content have been determined as stress indicators.

Tocopherol content

Tocopherols are the best known antioxidants in nature to protect lipids from oxidation (Burton and Ingold 1981; Min and Boff, 2002). In photosynthetic organisms, tocopherol levels are elevated in response to a variety of abiotic stresses, including high-intensity light (HL; Muller et al., 2003), drought, toxic metals (Luis et al., 2006), and high and low temperatures (Bergmuller et al., 2003). Vitamin E comprises a class of lipid-soluble molecules (α-, β-, δ-, and γ-tocopherols and tocotrienols) that are essential nutrients for mammals (Schneider, 2005). Tocopherols are only produced by photosynthetic organisms, including all plants, algae and most cyanobacteria (Horvath et al., 2006).

In the present study, a non-significant increase of the α-tocopherol content in both maize and oilseed rape leaves was found by graded REE-fertilizer application rates. The relationship between α-tocopherol content in maize and oilseed rape leaves and concentration of REEs in both maize and oilseed rape leaves was not significant. The highest tocopherol content was determined for oilseed rape (194.2 – 248.3 μg g^{-1} DW), while values for maize were distinctly lower (59.4 – 95.1 μg g^{-1} DW).

Tocopherol levels in oilseed rape are strongly affected by environmental factors. Marquard (1976, 1990) and Marwede et al. (2004) showed significant effects of location, temperature and light exposure and identified genotype environment interactions as a major source of variation in tocopherol content. The average of tocopherol content of winter oilseed rape was 81.9, 146.1 and 228.9 μg g^{-1} DW for α-, γ- and total tocopherol content, respectively (Marwede et al., 2005).

Total chlorophyll content

On the basis of their chemical structures, pigments can be classed into four families, i.e. tetrapyrroles (e.g. chlorophyll), carotenoids (e.g. β-carotene), polyphenolic compounds (e.g. anthocyanins), and alkaloids (e.g. betalains). Chlorophyll is a green pigment found in most plants, algae, and cyanobacteria. Chlorophyll is vital for photosynthesis, which allows plants to obtain energy from light.

The effects of REEs on plant photosynthesis have been investigated by many researchers (Xie and Chen, 1984; Xiong 1986; Gao and Xia, 1988; Bai and Deng, 1995; Xiong et al., 2000). At concentrations of more than 15 μg g^{-1} La, a decrease in chlorophyll contents as well as in chlorophyll a and b was observed in oilseed rape (Zeng et al., 2001). In tea plants, REE fertilizers enhanced photosynthesis (Wang et al., 2003e). Another study demonstrated that REEs might increase the translocation of photosynthetic products by 17-149% (Xiong, 1986). Inhibitory effects were also reported after oilseed rape plants were treated with La at high levels (> 300 μg g^{-1}). Higher doses (> 600 μg g^{-1}) even presented toxic effects (Zeng et al., 2001).

In general, in the present investigation the total chlorophyll content in maize and oilseed rape leaves decreased with increasing of REE application rates. This may be due to disturbance of chlorophyll biosynthesis or its degradation caused by lipid peroxidation (Somashekaraiah et al., 1992). Furthermore, the reduction in soluble protein content was probably due to toxic effects of ROS, which are especially prone to attack protein, resulting in protein degradation (Davies, 1987). Protein degradation might also result from higher activity of proteases activated under metal stress (Palma et al., 2002).

Higher chlorophyll contents were found in leaves of oilseed rape leaves (10.2–13.8 µmol g^{-1} DW) than maize (6.9-8.5 µmol g^{-1} DW). The relationship between total chlorophyll content in leaves of oilseed rape and REEs (La, Ce, Pr, and Nd) concentrations in roots and shoots was not significant for oilseed rape. The relationships were positive for maize but only for the relationship between Pr content and chlorophyll content in leaves it proved to be significant. The high variation within replicates (see Table B.42, Appendix) reveals that a higher number of replicates are required to work out the effect of REEs on enzyme activities.

5.3 Evaluation of chances and ecotoxicological risks of REEs in agriculture

Man's activity has substantially changed our environment through huge exploitation of energy and through substantial chemical activity. This has resulted in a massive redistribution of a variety of elements on the earth's surface.

The principal objective of a sustainable land-use system should be to exclude, or if not possible minimize risks to an acceptable level. Sustainability is intimately linked to soil quality, which must be maintained or enhanced.

To evaluate chances and risks of REEs in agriculture, it could be done by explaining the effects of REEs on the environment as for example soil fertility and assessing the possible mode of action of the toxicity of REEs.

The results of the present study revealed that neither in maize, nor in oilseed rape graded rates of individual and combined REEs showed any acute toxicity symptoms in plants, or even caused die-off. But it was clearly demonstrated that REEs applied at higher rates may hamper crop productivity. Changes in stress-related enzyme activities, though not significant, suggest that higher uptake and translocation of REEs induces stress reactions.

Impact of REEs on the environment

The application of REEs to industry and agriculture is constantly increasing, which consequently leads to scattering and bioaccumulation of REEs in the environment (Redling, 2006). Thus, REEs may influence the plant and soil ecosystem including the aquatic environment. Furthermore REEs may also affect animals, and last but not least, human beings through accumulation along the food chain. Systematic research into the environmental biogeochemical behavior of REEs in soil-plant systems is not satisfactory at present and information on the fundamental mechanisms in plant metabolism as well as on the effects of

REEs in humans after oral uptake is still lacking. Thus, until now, the ecological consequence of REE fertilization is not predictable. Further research might be advised prior to the application of REEs as either fertilizer to plants or feed additives to animals (Redling, 2006).

Effects of REEs on soil fertility

The influence of exogenous La on fertility parameters of red soil and paddy soil was studied by Cao et al. (2001). The results showed that with increasing amount of the added La, the proportion of exchangeable La in soils increased and that more exchangeable La was in red soil than in paddy soil. When the concentration of La was higher than 600 µg g^{-1}, the proportion of exchangeable La almost remained constant. When the concentration of La was lower than 1200 µg g^{-1}, no significant effect on CEC in red soil was determined. But when the concentration of La was higher than 1200 µg g^{-1}, it significantly increased/decreased the CEC in paddy soil.

From the present study, with increasing of the REE applications the soil EC increased and this affected soil microbiological parameters.

Many reports showed that soil microorganisms and material transformations are influenced by heavy metals (Hu et al., 1990), and some reports also showed that microbial activities are affected by REEs (Chu et al., 2002b). La had a stimulative effect on the nitrification and P transformation in red soil when the concentration of La was below 100 and 300 mg kg^{-1}, respectively; the higher concentration had an inhibitory effect and the inhibition was strengthened with increasing La concentration. La inhibited strongly the phenol decomposition in red soil and the inhibition is strengthened with increasing concentration of La (Chu et al., 2002a).

Effects of REEs on plant uptake

Investigations on the transfer of REEs along with the food chain into humans are still very rare. Concentrations of REEs determined in vegetable (0.05 - 2 µg g^{-1}) were very low. In the present investigation the application of graded REE fertilizer resulted for instance in a La concentration of up to 0.8 µg g^{-1} in shoots of maize and 1.6 µg g^{-1} in oilseed rape the total REE concentrations was 1.88 µg g^{-1} in maize and 3.41 µg g^{-1} in oilseed rape shoots (see Table B.6 in Appendix). In China, acceptable daily intake of REEs in nitrate form of 0.2-2 µg g^{-1} was reported to exceed the daily intake of 1.75-2.25 mg $person^{-1}$ day^{-1} of vegetable edibles. Consequently, the risk for humans to accumulate REEs through consuming vegetable comestible may be considered negligible (Redling, 2006).

Kučera et al. (2007) studied the distribution of REEs in soils and agricultural crops to assess the possible health risk for contamination of foodstuff. The highest REE concentrations of the crops were found in wheat chaff followed by lucerne and wheat corn. Among the fruits analyzed, the highest REE levels were determined in wine grapes, especially for Ce and Eu. Concerning vegetables, the highest REE concentrations, of all agricultural products studied, were found in parsley roots.

REEs applied to the soil may behave in the following ways:

(1) When applied in easily soluble form they are taken up by plants (this is the utilized fraction);

(2) They remain in available form but are not taken up by plants and thus prone to leaching;

(3) They are fixed in the soil;

(4) They are lost from the root space by migration processes.

Thus, only part of the applied REEs is recovered by plants. The utilization rate is a factor which describes REE uptake in relation to fertilizer dose (Finck, 1982):

$$\text{Utilization rate (\%)} = [(\text{REE removal} - \text{REE removal from soil reserves})/(\text{REE in product} + \text{natural plant available REEs in soil})] \times 100.$$

Table 5.2 shows the utilization rate of REEs by maize and oilseed rape whereby the rate was calculated separately for the shoot biomass and total biomass (roots and shoots).

In general, the utilization rate of all REEs decreased with increasing of graded REE-fertilizer application rates for maize and oilseed rape shoots (Table 5.2).

Table 5.2: Influence of graded REE applications on mean of REEs utilization rates (%) of shoots (μg g^{-1}) of maize and oilseed rape 66 days after sowing (2006)

REE-fertilizer application rates (μg g^{-1})	**Utilization rate (%) for maize shoots**				**Utilization rate (%) for oilseed rape shoots**			
	La	**Ce**	**Pr**	**Nd**	**La**	**Ce**	**Pr**	**Nd**
2.7	- 8.1	- 58.1	----*	11.8	5.4	- 2.9	- 13.8	0.0
27	6.4	5.4	----*	2.5	20.0	26.9	0.0	7.9
135	4.8	4.3	----*	1.5	14.6	21.6	1.8	8.0
270	4.8	4.6	----*	1.6	12.1	18.2	1.7	6.5
	Utilization rate (%) for maize shoots and roots				**Utilization rate (%) for oilseed rape shoots and roots**			
2.7	127	242	44.8	123	94.6	14.3	- 10.3	- 8.8
27	171	308	31.6	99.6	268	398	38.6	120
135	156	256	25.8	80.8	278	420	40.6	125
270	138	199	19.8	61.0	179	253	23.5	71.8

*< lower limit of quantitation

It was noticed that some values are negative indicating that the amount of REE taken up by plants of the control was higher than that of plants which received a REE dose. In comparison, values of >100%, which were regularly found for the total biomass (roots and shoots) show that the plants took up more REEs than were added to the soil. This means that in case of La and Ce, both elements were taken up constantly from sources other than plant available and added doses. This effect was apparently more pronounced at medium REE rates.

In the present investigation about 1.6-11.8% and 5.4-26.9% of REEs were taken up by oilseed rape and maize shoots (Table 5.2). Values below 100% for the total biomass of the crops indicate an increased risk of REE losses to the environment, for instance by leaching. This risk also exists after decomposition of roots after harvest and final release of soluble REEs.

Possible mode of action or mechanism of REEs toxicity

Several interactions between REEs and biological systems are known (Figure 5.7). There are conflicting evidence and opinions regarding the importance of REEs in pedology and biology. During the last decade much new information has appeared on the occurrence, behavior and possible biological role in soil and plant systems (Tyler, 2004).

The mechanisms of the toxic actions of REEs in biological systems known so far include (Gale, 1975; Rogers et al. 1980; Clarke and Hennessy, 1981; Martin, 1983; Plaha and Rogers, 1983; Washio and Miyamoto, 1983; Bierkens and Simkiss, 1988; Corzo and Sanders, 1992; Cheng et al. 1997; Leppe, 1997; Haftka and Weltje, 1999; Redling, 2006; Zohravi, 2007):

(1)- Competition between Ca/Mg and La, disrupting for instance bone-integrity and cellular signaling;

(2)- Replacement of Ca/Mg;

(3)- Reaction with proteins in which Ca/Mg are not usually involved;

(4)- Substitution of Fe by Sc;

(5)- Substitution of other elements;

(6)- Lipid–peroxidation due to redox cycling of REE that can exist in more than one oxidation state;

(7)- Phosphate deficiency, due to precipitation of phosphate–REEs with a very low solubility.

Wang et al. (2007) observed that proline accumulated in treated plants with La and Ce. This might be attributed to the strategies adapted by plants to cope with La and Ce toxicity, because proline can act as a reactive oxygen species (ROS) scavenger, an inhibitor of lipid peroxidation and a protein stabilizer (Mohanty and Matysik, 2001). REEs (La and Ce) induced oxidative stress by decreasing the activities of superoxide dismutase (SOD) and catalase (CAT) as well as by stimulating ROS production, resulting in lipid peroxidation and reduced chlorophyll and protein contents in *H. verticillata*. Like many heavy metals, La and Ce also caused oxidative damage in plants and may be considered a new type of pollutants.

In the present investigation significant negative correlations were found between REEs (La, Ce, Pr, and Nd) and B and Fe in oilseed rape roots and REEs (La, Ce, Pr, and Nd) and K in maize roots (Tables B.30, and B.31 in Appendix). Significant positive correlations were found for REEs and Mn, Cu, and S and B, Zn, Cu, Fe, Mg, and S for oilseed rape and maize, respectively.

For shoots, in case of maize significant negative/positive correlations were found between REEs and Zn, Mn, Fe, Ca, K and S. In case of oilseed rape significant negative/positive correlations were found between REEs and Mn and Fe. These correlations between REEs and plant nutrients might be a hint towards uptake and translocation antagonisms and synergisms, respectively.

From the results of the present study, it can be concluded that REE applications do influence soil micro-organisms, do influence plant growth and do influence mineral plant composition.

6 Summary/Zusammenfassung

Data on the biological effects of REEs are scarce and contradictory. There are no indications that REEs are essential to humans and animals. For plants, no data concerning essentiality are available either. It has been suggested that REEs may increase the yield of crop plants. However, the reported effects of application of REEs as fertilizers ranged from stimulation to no role in increasing agricultural plant production up to reduction of growth, apparently as a function of concentration, speciation and bioavailability.

The main objective of the present study was to investigate the effect of the REEs (La, Ce, Pr, and Nd) in a soil substrate on morphological, agronomic and physiological parameters of oilseed rape and maize, and soil microbial parameters under controlled greenhouse conditions. The research strategy was based on the comparison between the effects of REEs compared to that of another heavy metal, Cu, and Ca as Ca may be replaced by the presumably more effective La in plant metabolism. Two agricultural crops, maize (*Zea mays* L.) and oilseed rape (*Brassica napus* L.) were tested. The investigations were conducted in pot experiments under controlled greenhouse conditions. Each pot (capacity 1 litre) contained 900 g of soil substrate (dry weight basis) and was seeded with 6 maize seeds and 10 oilseed rape seeds on April 29th and Mai 14th and harvested on July 5th and July 17th in 2005 and 2006, respectively.

Several treatments have been performed using five different REE-fertilizer application rates (REE0: control, REE1: 2.7 µg g^{-1}, REE2: 27 µg g^{-1}, REE3: 135 µg g^{-1} and REE4: 270 µg g^{-1} added as $RECl_3 \times xH_2O$). REE-fertilizer (La, ce, Pr, Nd), La, Ce, Ca and Cu treatments were applied at rates being multiples of their plant available content in soils (1-fold, 10-fold, 50-fold, 100-fold). In case of Ca graded rates were based on its plant available concentration in the first year of experimentation and adjusted to that of rare earth elements in the second year of experimentation. Essential nutrients (N, P, K, Mg, and S) were mixed homogenously with the soil before sowing in order to fully satisfy the nutrient demand. Each treatment was carried out with 4 and 6 replicates.

The most important findings of the research work presented here were:

1) With graded REE-fertilizer application rates, the soil enzyme activities (dehydrogenase and alkaline phosphatase) decreased. In general, the dehydrogenase activity was 78 % higher in 2005 and 96% higher in 2006 in vegetated (maize) soil compared to non-vegetated soil. The corresponding values for oilseed rape were 84% in 2005 and 96% in

2006. With graded Ca (at rates based on its plant available concentration) and Cu application rates, the soil enzyme activities (dehydrogenase and alkaline phosphatase) decreased, whereby this effect can be attributed to the toxic effect of Cu to soil microorganisms. The strongest Ca effect was observed in 2005 when maize was cultivated on the dehydrogenase activity with a reduction of 24%. In comparison, Cu yielded a reduction of the dehydrogenase activity of 56% when maize was grown and 62% when oilseed was cultivated. Ca reduced the alkaline phosphatase activity at maximum by 25% when oilseed rape was grown in 2005. Cu reduced the alkaline phosphatase activity by about 17% in both crops. Generally, soil enzyme activity values (dehydrogenase and alkaline phosphatase) of oilseed rape were between 25 and 38% higher than for maize.

2) Low rates of La, Ce and REE-fertilizer applications resulted regularly in a higher number of selected microbial counts, whereby this effect was more pronounced for maize. Also Ca rates equivalent to that of La and Ce yielded a significant increase in the number of heterotrophic bacteria and actinomycetes in maize pots.
3) Graded REE-application rates promoted (at low levels) and inhibited (at high levels) the soil microbial communities and this observation is well in accordance with the literature. Graded REE-fertilizer decreased significantly the number of fungi in pots grown with oilseed rape from $1.5 \cdot 10^6$ to $6.9 \cdot 10^5$, while this effect was not significant for maize. Graded rates of Cu reduced all three microbial parameters irrespective of the crop. This may be attributed that graded Cu application rates are toxic at these levels to soil microbial communities. Fungi, among soil microbial communities, were more sensitive to changes in soil characteristics. This may be related the negative and significant correlative relationships between the number of fungi and soil EC and pH and some soil enzyme activities.
4) Graded REE applications, in general, decreased the germination rate from 100% to 83% and plant height from 73 cm to 52 cm in case of maize. In case of oilseed rape, plant height was reduced from 29.7 cm to 22.1 cm. The results were consistent in each year. The results revealed that the effect on germination rate (maize) and plant height (oilseed rape) was significant when the highest rate of REE fertilizers (270 $\mu g\ g^{-1}$) were applied.
5) It was observed that graded REE-fertilizer application rates promoted the total biomass production up to levels of 2.7 $\mu g\ g^{-1}$ for maize in 2005 and 2006, and 27 $\mu g\ g^{-1}$ in 2005 and 2.7 $\mu g\ g^{-1}$ for oilseed rape. So the biomass of maize increased in 2005 from 15.5 g pot^{-1} to 24.9 g pot^{-1} and in 2006 from 14.0 g pot^{-1} to 31.5 g pot^{-1}. In case of oilseed rape the

biomass increased from 10.0 g pot^{-1} to 20.9 g pot^{-1} in 2005 and 12.5 g pot^{-1} to 13.8 g pot^{-1} in 2006.

Biomass production of both crops was reduced at rates of 270 µg g^{-1} by up to 47% in maize and 52% in oilseed rape. This observation is well in accordance with results reported in literature. These and other findings suggest that next to the concentration, the composition of REEs influence the impact on plant growth.

6) The REE content of roots and shoots increased with increasing REE applications (La, Ce and REE-fertilizer). The highest concentration of REEs was found in roots when compared to shoots of oilseed rape and maize. The La, Ce, Pr and Nd content was at maximum 120, 180, 17.9 and 56.7 µg g^{-1} in roots and 1.7, 1.8, 0.18 and 0.58 µg g^{-1} in shoots of maize. The upper values for oilseed rape were 163, 235, 21.9 and 67.2 µg g^{-1} in roots and 3.7, 5.7, 0.61 and 2.0 µg g^{-1} in shoots. On average the La, Ce, Pr and Nd concentrations were 100 times higher in roots than in shoots of maize. Differences in the shoot concentrations between both crops were even more pronounced for Ca and Ce, which were about 10 times higher in oilseed rape than maize. The Pr and Nd concentration in oilseed rape shoots was with 0.61 and 2.0 µg g^{-1} about 27 and 2.5 times higher than in maize. This may be attributed to the fact that roots of dicots (oilseed rape) release and take up more REEs in the soil from its compounds than monocots (maize). The results reveal that next to crop also element-specific differences in root uptake of REEs exist and that translocation of individual REEs within the plant seem to be controlled by different transporter systems for oilseed rape and maize.
7) Accumulation of REEs in different parts of plants decreased in the following order: root > shoots and REEs in the order: Ce > La > Nd >Pr for each part of plants and for each crop. With increasing application rates of La, Ce and REE-fertilizer the concentration and uptake of La, Ce and REEs (La, Ce, Pr and Nd) increased in both roots and shoots of each crop.
8) Highly significant and significant correlation coefficients (r) were found between graded REE-application rates and the REE uptake of shoots and roots in maize and oilseed rape. The relationship between Ca concentration in maize roots and REE concentrations in maize roots proved to be not significant. In contrast, these relationships were significant between REE concentrations in maize shoots and Ca concentrations in the same plant part.
9) In general, with the exception of K, graded REE-fertilizer applications increased the concentration of essential nutrients from about 15% for S to up to 45% for Zn in roots of maize. This trend was not consistent for oilseed rape. With graded REE-fertilizer

application rates, the concentrations of K, Fe, and Zn decreased in shoots of maize and oilseed rape. In case of roots, the highest uptake values were found for all essential macro and micro-nutrients in maize, whereas that for oilseed rape were least affected by graded REE-fertilizer application rates. Inverse results were determined for shoots where the S, Ca and Mn uptake was highest for oilseed rape and distinctly lower in maize.

10) The individual transfer factors (TFs) of REEs decreased with graded REE-fertilizer application rates for roots and shoots of maize and oilseed rape. The highest application rate of REE fertilizer reduced the $TF_{soil/roots}$ in pots vegetated with maize from 4.24 to 1.19 (La), 11.0 to 2.2 (Ce), 4.5 to 0.9 (Pr) and 4.7 to 0.8 (Nd); the $TF_{soil/shoots}$ decreased from 0.096 to 0.017 (La), 0.283 to 0.022 (Ce) and 0.084 to 0.008 (Nd). The highest application rate of REE fertilizer reduced the $TF_{soil/roots}$ in pots vegetated with oilseed rape from 9.54 to 1.52 (La), 23.9 to 2.9 (Ce), 9.4 to 1.1 (Pr) and 9.7 to 0.95 (Nd); the $TF_{soil/shoots}$ decreased from 0.225 to 0.037 (La), 0.468 to 0.07 (Ce), 0.51 to 0.031 (Pr) and 0.182 to 0.029 (Nd). Generally, for individual REEs the TF values decreased in the order Ce > La > Nd > Pr in roots and shoots of oilseed rape and maize. The TF for total biomass (roots or shoots) decreased with graded REE-fertilizer application rates for both crops. In general, TFs for individual REEs and the sum of REEs were higher when oilseed rape was grown than maize; this result was consistent for roots and shoots.

11) When compared to maize, oilseed rape plants contained the highest values of both α–tocopherol (248 µg g^{-1} dw) and total chlorophyll (13.8 µmol g^{-1} dw) when treated with REEs. This indicates that monocotyledonous plants (like maize) react differently to heavy metal stress than dicotyledonous plants. Graded REE-fertilizer application rates increased the α-tocopherol content in maize from 59 to 95 µg g^{-1} dw, too but this effect was not significant for any crop. The total chlorophyll content, in maize and oilseed rape leaves decreased with increasing of graded REE application rates.

Ein Beitrag zur Wirkung von Seltenen Erden im System Boden/Pflanze

Zusammenfassung

Daten zur biologischen Wirksamkeit von Seltenen Erden sind nur begrenzt verfügbar und widersprüchlich. Es gibt keinerlei Hinweise, dass Seltene Erden lebensnotwendig für Menschen, Tiere und Pflanzen sind. Verschiedene Untersuchungen in der Literatur zeigen, dass die Zufuhr von Seltenen Erden in Abhängigkeit von deren Pflanzenverfügbarkeit, chemischer Speziierung und Höhe der Zufuhr den Ertrag steigerte und senkte bzw. ohne Einfluss blieb.

Ziel der vorliegenden Arbeit war es, den Einfluss Seltener Erden (La, Ce, Pr, Nd) auf morphologische, agronomische und physiologische Parameter von Raps und Mais sowie mikrobiologische Bodenmerkmale unter kontrollierten Bedingungen im Gewächshaus zu quantifizieren. Hierbei wurde die Wirkung einzelner Elemente der Seltenen Erden mit einem Düngemittel, welches La, Ce, Pr und Nd enthielt, einem essenziellen Schwermetall, Kupfer und Ca, welches vermutlich durch das physiologisch wirksamere Lanthan ersetzt werden kann, vergleichend gegenübergestellt. Zwei landwirtschaftliche Kulturen, Mais (*Zea mays* L.) und Raps (*Brassica napus* L.) wurden als Versuchspflanzen gewählt. In den Gewächshausversuchen wurden Gefäße mit 1 L Fassungsvermögen eingesetzt und jeweils mit 900 g Boden befüllt. Insgesamt 6 Mais- und 10 Rapssamen wurden am 29. April 2005 bzw. 14. Mai 2006 eingesät und am 5. Juli 2005 bzw. 17. Juli 2006 beerntet.

Insgesamt wurde ein Gemisch an Seltenen Erden (La, Ce, Pr, Nd) in Form eines chinesischen Düngemittels in den folgenden Stufen appliziert: (REE0: Kontrolle, REE1: 2.7 $\mu g\ g^{-1}$, REE2: 27 $\mu g\ g^{-1}$, REE3: 135 $\mu g\ g^{-1}$ und REE4: 270 $\mu g\ g^{-1}$, in chloridischer Form als $RECl_3 \times xH_2O$) zugeführt. Düngemittel sowie La, Ce, Ca und Cu wurden jeweils als Vielfaches ihrer pflanzenverfügbaren Konzentrationen im Boden ausgebracht (Kontrolle, 1-fach, 10-fach, 50-fach, 100-fach). Im Fall von Ca erfolgte die Zufuhr auf Basis der verfügbaren Gehalte im ersten Versuchsjahr und entsprechend der verfügbaren Gehalte an Seltenen Erden im Boden im zweiten Jahr. Essenzielle Nährstoffe (N, P, K, Mg und S) wurden vor Einsaat sorgfältig mit dem Boden vermischt, um den Bedarf der Pflanzen sicherzustellen. Jede Behandlung hatte 4 bzw. 6 Wiederholungen.

Die wichtigsten Ergebnisse der vorliegenden Arbeit lassen sich wie folgt zusammenfassen:

1) Eine gesteigerte Zufuhr des Seltene Erden Düngemittels reduzierte die Enzymaktivitäten (Dehydrogenase und alkalische Phosphatase) im Boden. So sank in den Varianten mit Mais die Dehydrogenase-Aktivität um 78% in 2005 und 96% in 2006. Für Raps betrugen die entsprechenden Werte 84% in 2005 und 96% in 2006. Bis auf wenige Ausnahmen waren in beiden Versuchsjahren die Enzymaktivitäten im bewachsenen Boden höher als im unbewachsenen. Steigende Ca- und Cu-Zufuhr führte zu einer Abnahme der Enzymaktivitäten (Dehydrogenase und alkalische Phosphatase), die im Fall von Cu auf dessen Toxizität zurückzuführen ist. Der stärkste Ca-Effekt trat bei Mais mit einer Reduzierung der Dehydrogenase-Aktivitäten um bis zu 24% auf. Im Vergleich hierzu reduzierte Cu die Dehydrogenase-Aktivität um bis zu 56% bei Mais und 62% bei Raps. Ca reduzierte die alkalische Phosphatase-Aktivität um bis zu 25% in den Varianten mit Raps in 2005. Cu reduzierte die alkalische Phosphatase-Aktivität um ca. 17% in beiden Kulturen. Generell waren beide Enzymaktivitäten um 25% (Dehydrogenase) und 38% (alkalische Phosphatase) höher, wenn Raps und nicht Mais angebaut wurde. Die Aktivitäten beider Enzyme waren höher in Böden auf denen Raps wuchs als in den Mais-Varianten.
2) Eine gesteigerte Zufuhr geringer Mengen des Seltene Erden Düngemittels sowie von La und Ce erhöhte regelmäßig die Aktivität ausgewählter mikrobieller Gemeinschaften im Boden, wobei dieser Effekt in den Mais-Varianten ausgeprägter war. Bei einer gesteigerten Ca-Zufuhr, die der von La und Ce entsprach, wurde ein signifikanter Anstieg der Anzahl heterotropher Bakterien und Actinomyceten in den Mais-Varianten bestimmt.
3) Die gesteigerte Zufuhr an Seltenen Erden erhöhte regelmäßig die Anzahl der mikrobiellen Gemeinschaften sofern geringe Mengen appliziert wurden, während hohe Dosen zu einer Reduzierung führten. Ähnliche Ergebnisse wurden zuvor in der Literatur beschrieben. Die gesteigerte Zufuhr des Seltene Erden Düngemittels reduzierte signifikant die Anzahl an Pilzen in Gefäßen mit Raps von $1{,}5 \cdot 10^6$ auf $6.9 \cdot 10^5$, wohingegen dieser Effekt bei Mais nicht signifikant war. Unabhängig von der Kulturart führte eine gesteigerte Cu-Zufuhr zu einer signifikanten Abnahme der Anzahl an Pilzen, Actinomyceten und heterotrophen Bakterien. Generell wurde festgestellt, dass Pilze am empfindlichsten auf die Behandlungen reagierten. Dies könnte in Zusammenhang mit den beobachteten signifikanten negativen Korrelationen zwischen Anzahl an Pilzen und pH sowie Leitfähigkeit und Enzymaktivitäten stehen.

4) Die Zufuhr gesteigerter Mengen an Seltenen Erden führte bei Mais in beiden Versuchsjahren und bei beiden Kulturen zu einer Abnahme der Keimrate von 100% auf 83% und eine Reduzierung der Wuchshöhe von 73 cm auf 52 cm. Die Wuchshöhe von Raps verringerte sich von 30 cm auf 22 cm. Vergleichbare Ergebnisse wurden in beiden Jahren gefunden. Dieser Effekt auf Keimrate (Mais) und Wuchshöhe (Raps) war signifikant bei einer Zufuhr des Seltene Erden Düngemittels in Höhe von (270 µg g^{-1}).
5) Eine gesteigerte Zufuhr des Seltene Erden Düngemittels erhöhte die Gesamtbiomasse-Produktion in beiden Versuchsjahren sofern die Mengen 2,7 µg g^{-1} bei Mais und 27 µg g^{-1} bzw. 2,7 µg g^{-1} bei Raps in 2005 und 2006 nicht überschritten. In 2005 stieg die Biomasse von Mais von 15,5 auf 24,9 g $Gefäß^{-1}$ und in 2006 von 14,0 auf 31,5 g $Gefäß^{-1}$. Im Fall von Raps führte die Behandlung zu einer Steigerung der Biomasse-Produktion von 10,0 auf 20,9 g $Gefäß^{-1}$ in 2005 und 12,5 auf 13,8 g $Gefäß^{-1}$ in 2006.

   Im Gegensatz hierzu reduzierte eine Aufwandmenge von 270 µg g^{-1} signifikant die Biomasseproduktion von Mais um bis zu 47% und von Raps um bis zu 52%. Diese Ergebnisse stimmen mit denen aus anderen Untersuchungen in der Literatur überein. Diese und andere Ergebnisse zeigen, dass die Wirkung von Seltenen Erden nicht nur konzentrationsabhängig ist, sondern auch durch deren Zusammensetzung beeinflusst wird.
6) Die gesteigerte Zufuhr an Seltenen Erden (La, Ce, Seltene Erden Düngemittel) führte zu einem Anstieg der Gehalte an La, Ce, Pr und Nd in Wurzeln und Blattmasse. Hierbei wurden die höchsten Konzentrationen in den Wurzeln von Raps und Mais bestimmt. Der jeweils höchste La-, Ce, Pr- und Nd-Gehalt in den Wurzeln von Mais lag bei 120 (La), 180 (Ce), 17,9 (Pr) und 56,7 (Nd) µg g^{-1} und in der oberirdischen Blattmasse bei 1,7 (La), 1,8 (Ce), 0,18 (Pr) und 0,58 (Nd) µg g^{-1}. Bei Raps betrugen die Maximalwerte 163 (La), 235 (Ce), 21.9 (Pr) und 67.2 (Nd) µg g^{-1} in den Wurzeln und 3,7 (La), 5,7 (Ce), 0,61 (Pr) und 2,0 (Nd) µg g^{-1} in der oberirdischen Blattmasse. Die La Ce, Pr und Nd-Gehalte waren durchschnittlich 100 Mal höher in den Wurzeln als in der oberirdischen Blattmasse von Mais. Unterschiede zwischen beiden Kulturen waren sehr ausgeprägt für Ca und Ce, wobei in Raps die Gehalte in der oberirdischen Biomasse ungefähr 10 Mal höher waren als in Mais. Die Pr- und Nd-Gehalte in der oberirdischen Blattmasse von Raps waren mit 0.61 und 2.0 µg g^{-1} ungefähr 27 bzw. 2,5 Mal höher als in Mais. Diese Unterschiede zwischen Raps und Mais sind auf kulturartspezifische Unterschiede bei der Aufnahme von Seltenen Erden durch monokotyle und dikotyle Pflanzen zurückzuführen. Die Ergebnisse zeigen, dass neben diesen kulturartabhängigen auch elementspezifische Unterschiede in der Aufnahme von Seltenen Erden in die Wurzel bestehen und dass deren Verlagerung in

oberirdische Pflanzenteile offenbar durch unterschiedliche Transporter in Raps und Mais kontrolliert werden.

7) Die Gehalte an Seltenen Erden waren in Wurzeln immer höher als in der oberirdischen Blattmasse. In den beiden Pflanzenteilen nahmen die Elementgehalte bei beiden Kulturen in der folgenden Reihenfolge Ce > La > Nd > Pr ab. Die gesteigerte Zufuhr an La, Ce und Seltene Erden Düngemittel erhöhte Konzentration und Aufnahme an La, Ce, Pr und Nd in beiden Pflanzenteilen und Kulturen.
8) Hochsignifikante und signifikante Korrelationen bestanden zwischen der Höhe der Zufuhr an Seltenen Erden und dem Gehalt an Seltenen Erden in Wurzeln und oberirdischer Blattmasse von Raps und Mais. Für Mais konnte keine signifikante Beziehung zwischen dem Ca-Gehalt und dem Gehalt and La, Ce, Pr und Nd in Wurzeln bestimmt werden. Im Gegensatz hierzu waren die entsprechenden Beziehungen in der oberirdischen Blattmasse signifikant.
9) Generell war die Zufuhr gesteigerter Mengen an Seltene Erden Düngemittel bei Mais mit höheren Gehalten an lebensnotwendigen Nährelementen, mit Ausnahme von K, in der Wurzelmasse verbunden, während ein solcher Zusammenhang für Raps nicht nachgewiesen werden konnte. So stieg der S-Gehalt um 15% und der Zn-Gehalt um bis zu 45%. Darüber hinaus nahmen die Gehalte an K, Fe und Zn in der oberirdischen Blattmasse von Mais und Raps ab. Die höchste Nährstoffaufnahme in Wurzeln wurde für Mais bestimmt, während die Gehalte in Raps nur geringfügig beeinflusst wurden. Im Gegensatz hierzu war die Aufnahme von S, Ca und Mn in die oberirdischen Blattmasse von Raps signifikant höher als bei Mais.
10) Die individuellen Transferfaktoren für La, Ce, Pr und Nd sanken mit steigender Zufuhr der Elemente in Wurzeln und oberirdischer Blattmasse beider Kulturen. Die höchste Rate an Seltene Erden Düngemittel führte zu einer Abnahme des $\text{Transferfaktors}_{\text{Boden/Wurzel}}$ in den Mais-Varianten von 4,24 auf 1,19 (La), 11,0 auf 2,2 (Ce), 4,5 auf 0,9 (Pr) und 4,7 auf 0,8 (Nd); der $\text{Transferfaktor}_{\text{Boden/Blatt}}$ sank von 0,096 auf 0,017 (La), 0,283 auf 0,022 (Ce) und 0,084 auf 0,008 (Nd). Im Vergleich hierzu führte die höchste Rate an Seltene Erden Düngemittel zu einer Reduzierung des $\text{Transferfaktors}_{\text{Boden/Wurzel}}$ in den Raps-Varianten von 9,54 auf 1,52 (La), 23,9 auf 2,9 (Ce), 9,4 auf 1,1 (Pr) und 9,7 auf 0,95 (Nd); der $\text{Transferfaktor}_{\text{Boden/Blatt}}$ sank von 0,225 auf 0,037 (La), 0,468 auf 0,07 (Ce), 0,51 auf 0,031 (Pr) und 0,182 auf 0,029 (Nd).

    Hierbei nahmen die Transferfaktoren in der Reihenfolge Ce > La > Nd > Pr ab. Die Zufuhr gesteigerter Mengen an Seltene Erden Düngemittel führte auch zu einer Abnahme der Transferfaktoren für die Gesamtbiomasse (Wurzeln plus oberirdische Blattmasse) in beiden Kulturen. Im allgemeinen waren die Transferfaktoren für einzelne Elemente (La, Ce, Pr, Nd) sowie deren Summe in Wurzeln und oberirdischer Blattmasse höher für Raps als für Mais.

11) Im Vergleich zu Mais, wurde in Rapsblättern nach Zufuhr von Seltenen Erden jeweils der höchste Gehalt an α–Tocopherol mit 248 $\mu g\ g^{-1}$ (TM) und Gesamtchlorophyll mit 13.8 $\mu mol\ g^{-1}$ (TM) bestimmt. Dies deutet darauf hin, dass monokotyle Pflanzen wie Mais sich in ihrer Reaktion auf Schwermetallstress von der dikotyler Pflanzen unterscheiden. Die gesteigerte Zufuhr an Seltene Erden Düngemittel erhöhte zwar auch den Gehalt an α–Tocopherol von Mais von 59 auf 95 $\mu g\ g^{-1}$ (TM), aber dieser Effekt war bei keiner Kultur signifikant. Der Gesamtchlorophyllgehalt in Blättern von Mais und Raps nahm mit steigender Zufuhr an Seltenen Erden ab.

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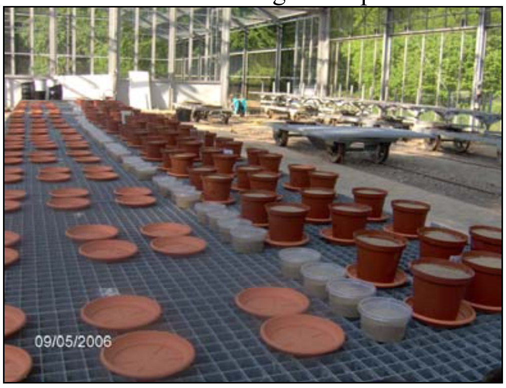
8 Appendix

A.1: *Preparing of the used soil*

Filling of the pots with used soil and essential nutrients



Preparing of the microbiological assessment pots (small ones)

A.2: *Preparing of the pots and different growth stages of the plants*

The sieved and used soil

Mixing soil with essential nutrients

Filling the pots with soil and essential nutrients

Emergence the seedling after cultivation

Appendix

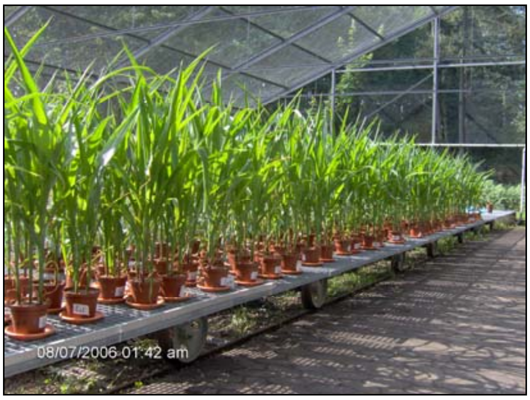
Vegetative growth of plants (after 5 days from cultivation)

After about 2 weeks

after about 18 days

After about 3 weeks

after about one month



After about 7 weeks

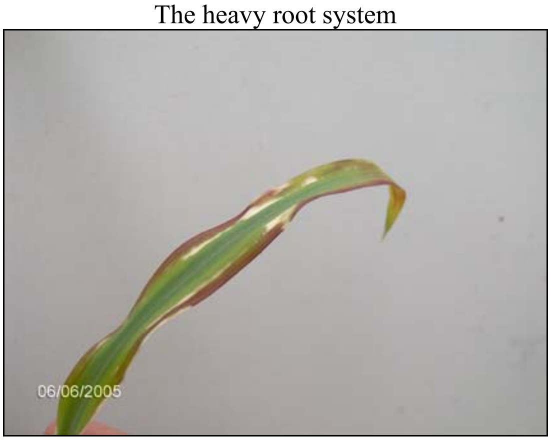
Appendix

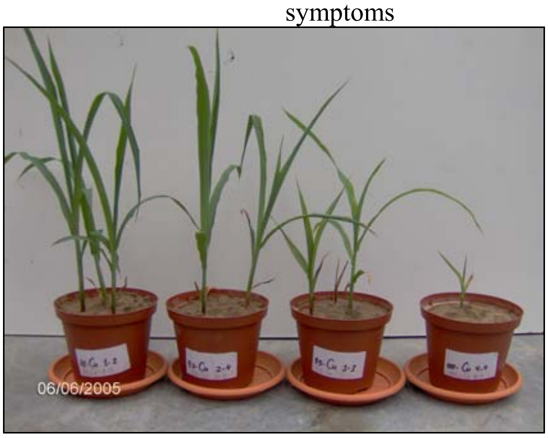
The second part of the experiment (non-vegetated soil)

A.3: *Some photos from the experiment*

The heavy root system

symptoms



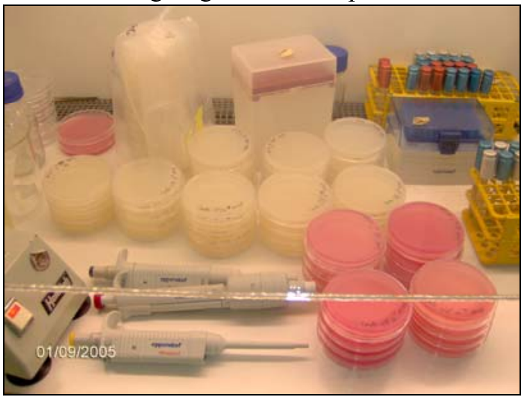


Copper toxicity

A.4: *Some Microbiological assessment steps which used during the study*

Shaking stage of soil samples

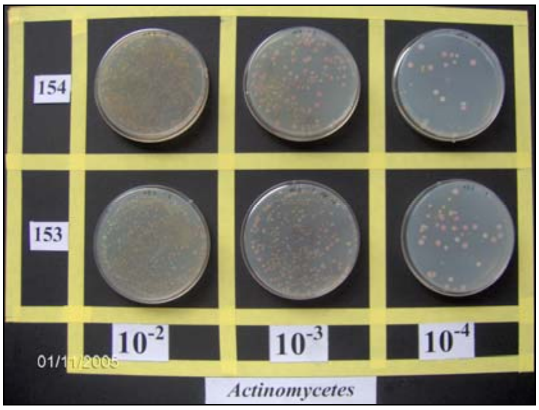
Drying of Petri dishes at clean bench



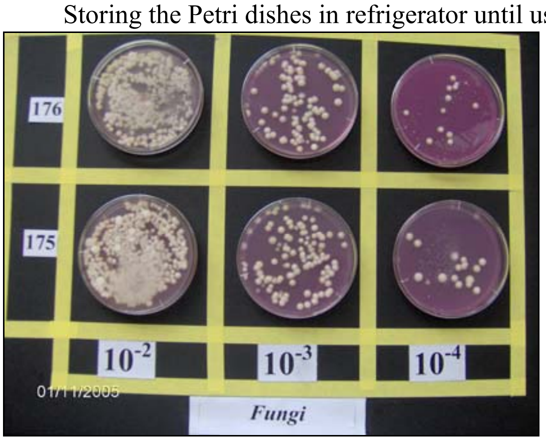
Preparing of samples to inoculation

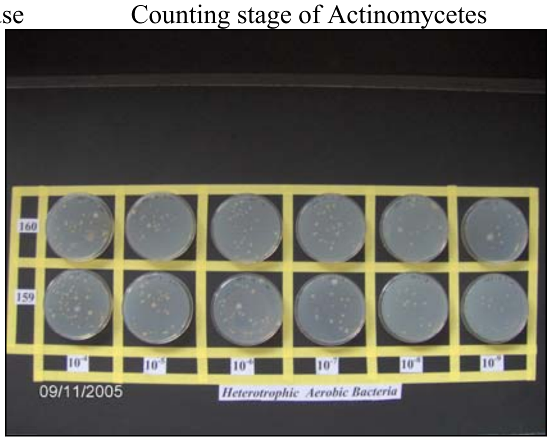
Inoculated Petri dishes at 20º for one or two weeks

Storing the Petri dishes in refrigerator until use

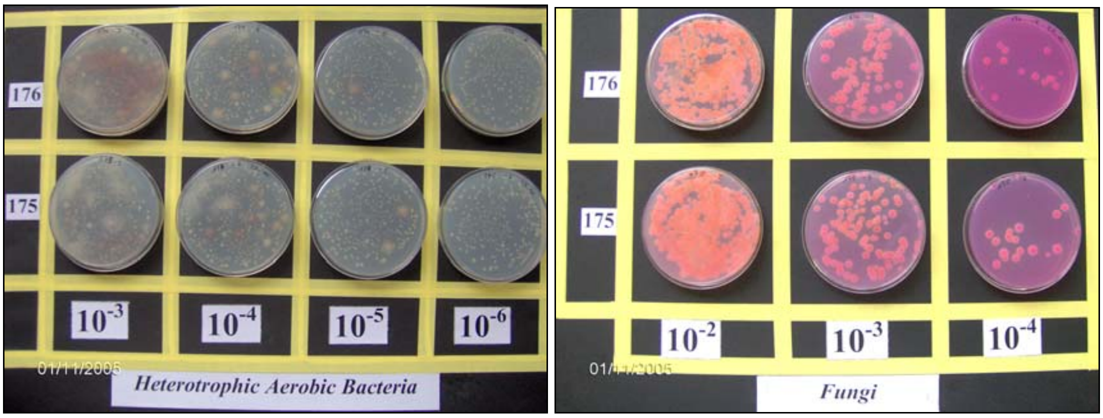


Counting stage of Actinomycetes





Counting stage of bacteria and fungi



Counting stage of bacteria and fungi

Sterilization of Petri dishes after counting using special plastic bags in autoclave

A.5: *At harvest*

Put the soil including roots in sieve 2 mm and remove carefully the roots

Collecting whole roots in each pot and cleaning with deionized water

Appendix

Dividing the soil to two parts, one for microbial analyses and other for chemical analyses

Leaf discs performance for some enzymatic assessments

Drying leaf discs after storing at -80ºC until analysis

Liquid N_2 usage for leaf discs

Experiment after harvesting the shoots

Storing of soil samples at temperature room for chemical analysis

Storing of samples at 4 ºC

A.6: *Enzymatic assessment in soil*

(1) *Dehydrogenase Enzyme Activity:*

Weighting stage

Filtration stage

Appendix

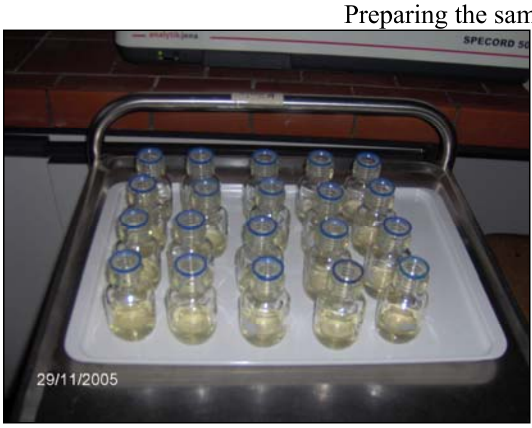
Measuring stage on spectrophotometer instrument

(2) ***Alkaline Phosphatase Activity:***

Weighting the soil samples

Adding the solution

Preparing the samples for filtration



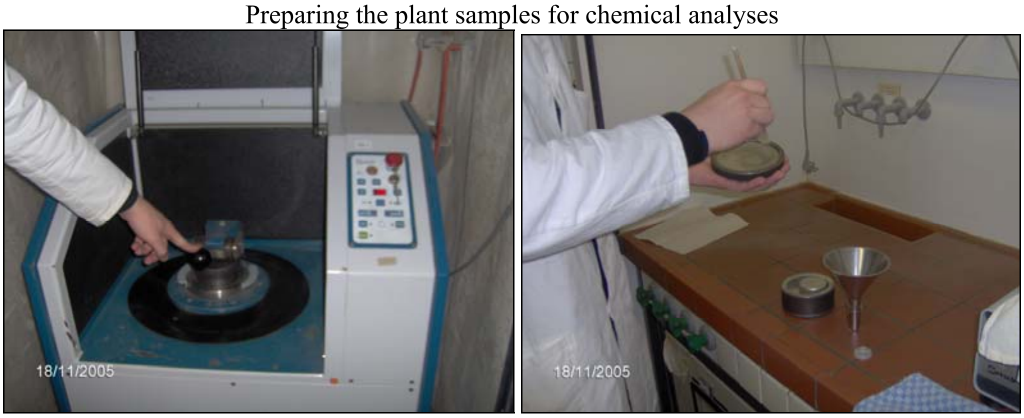
Measuring stage on spectrophotometer instrument

D.7: *Some chemical assessments*

Measuring of pH (soil acidity) and EC (soil salinity)

A.8: *Plant samples preparing*

Preparing the plant samples for chemical analyses



Grinding stage of plant samples

Cleaning stage after each plant sample

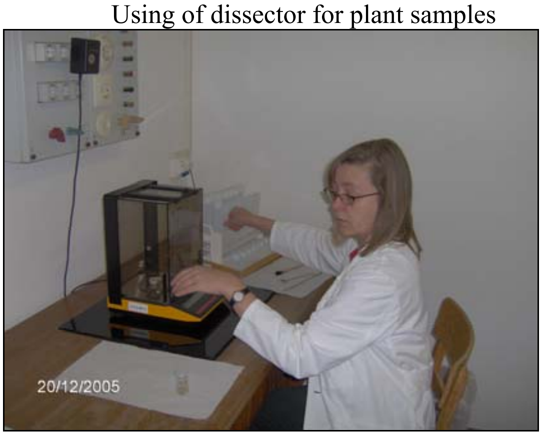
Another instrument used for plant sample grounding (small amounts)

A.9: *Plant samples Analyses*

Drying of plant samples in the oven at 45ºC

Using of dissector for plant samples

Drying of the used materials in the oven after washing and before usage

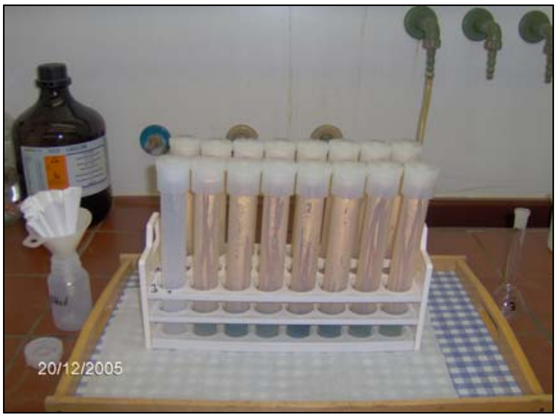


Weighing of the plant samples

Adding of H_2O_2 and HNO_3 to samples

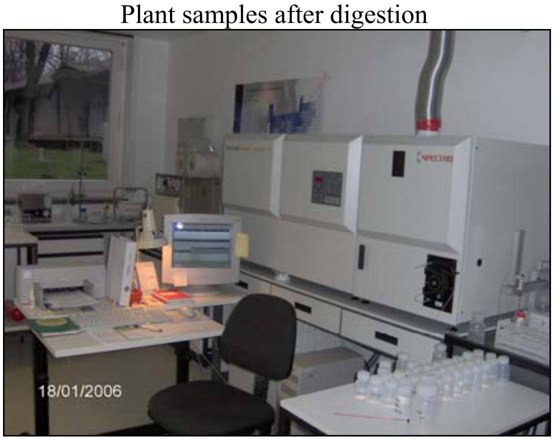
Using of the microwave

Appendix



Plant samples after digestion

Filtration of the digested samples



ICP-OES instrument

ICP-QMS instrument

Appendix

Table A.1: Historical review on research and development of scandium (adapted from Horovitz, 1990)

Year	Event	Reference
1869	Prediction of an unknown element, “eka-boron”	Mendeleev
1879	Discovery in euxenite & gadolinite	Nilson
1879	Preparation of 1.2 g scandium oxide	Cleve
1898	Estimate of lithosphere abundance	Vogt
1908	Patent for scandium separation from minerals	Meyer
1909	Detection in the solar system	Fowler
1911	True scandium mineral Thortveitite discovered	Schetelig
1914	Scandium ß-diktonate [$Sc(acac)_3$] prepared	Morgan
1923	100% atomic mass of ^{45}Sc measured	Aston
1924	Magnetic resolution of scandium lines	Goudsmit and Zeeman
1925	Detection in plant material	von Lippmann
1928	Effect of mouse carcinoma	Ishiwara
1935	Identification of scandium isotopes	de Hevesy
1937	Scandium biochemistry studied	Beck
1937	Preparation of metallic scandium	Fischer et al.
1938	Detection in animals	Lux; Noddack
1939	Specific growth stimulation of Asperigillus	Steinberg
139	Bone micrographs with scandium X-rays	Dershem
1942	Intensive biochemical studies	Durbin
1946	^{46}Sc publicly available	Ames Lab.
1947	Inhibition of thromboplastic effect	Chargaff and Green
1948	Uses of ^{46}Sc as environmental tracer	Arrol
1957	Biochemistry in man and animals	Spencer et al.
1961	High purity scandium metal produced	Daane
1962	Binary alloys studied	Gschneider, Jr.
1963	Single scandium crystals prepared	Savitsky et al.
1965	Stimulation of plants growth	Horovitz
1966	Identification of ^{51}Sc	Erskine et al.
1972	Scandium metal used in ion microprobe mass analysis	Guthrie and Blewer
1973	Preparation of 99.9 atomic Sc	Spedding and Croat
1982	^{46}Sc labeled MAb for tumor imaging	Scheinberg et al.
1992	Fast hydrolysis of RNA	Korniyama et al.
1996	Sc-chelate conjugated MAb injected to a patient	Scheinberg

Appendix

Table A.2: Historical review on research and development of yttrium (adapted from Horovitz, 1990)

Year	Event	Reference
1787	Mineral ytterbite discovered in Sweden	Arrhenius
1794	Rare earth ytterbia isolated	Gadolin
1828	Identification of yttrium metal	Woehler
1832	Yttrium salts and yttrium minerals studied	Berzelius et al.
1843	Yttrium separated from terbium	Mosander
1886	Fractionation of yttrium group	Crookes
1907	Pharmacological study on animals	Bachem
1908	Chemistry of yttrium compounds	Lenher
1910	Physiology and toxicology in animals	Mines
1913	Anticoagulant effect in blood	Frouin
1914	Inhibitory effect on plants	Evans
1923	100% atomic mass of ^{89}Y measured	Aston
1927	Effect on mouse carcinoma	Ishiwara
1931	Cancer therapy in animals	Maxwell and Bischoff
1932	Structure of metallic yttrium	Quill
1938	Hickory plant –yttrium accumulator	Robinson
1942	Artificial ^{90}Y produced	Manhattan Project
1946	^{90}Y publicly available	Ames Lab.
1946	Absorption and retention by organisms	Berkeley Lab.
1947	^{90}Y used in plant nutrition studies	Stout et al.
1949	Colloidal properties of yttrium radioisotopes	Gofman
1950	Large yttrium ingots prepared	Ames Lab.
1953	Metabolism of ^{90}Y	Kawin
1955	Effect of ^{90}Y on plants	Rediske and Selders
1955	Biochemistry in man and animals	Rosoff et al.
1956	Therapeutic use of ^{90}Y	Copp & Kawin
1957	Metabolism of ^{90}Y in animals	Boroughs et al.
1959	Single yttrium crystals prepared	Carlson et al.
1964	^{90}Y marked micro spheres for cancer therapy	Ariel
1970	Superconductivity in yttrium at high pressure	Wittig
1970	^{90}Y used for human knee effusions treatment	Prichard et al.
1972	Complexes with carbohydrates	Angyal
1985	^{90}Y labeled MAb for radiotherapy	Hnatowich
1988	First 90K superconductor $YB_2Cu_3O_7$ discovered	Wu et al.
1992	Fast hydrolysis of RNA	Komiyama et al.

Table A.3: Results for the lanthanides, Th and U in soils and agricultural crops by INAA and RNAA (in ng.g^{-1}, dry mass, unless otherwise stated)[a,b] (adapted from Kurčera et al., 2007)

Element	Method	Soil, µg g^{-1} (N= 5)	Wheat (N=3)	Wheat chaff (N=3)	Lucerne (N=3)
La	INAA	**41.9** (24.6-46.9)	**26** (16-39)	**124** (85-285)	**95** (61-154)
Ce	INAA	**72.6** (42.7-81.7)	**44** (39-49)	**169** (96-461)	**181** (71-216)
Pr	INAA	**11.5** (< 9-11.5)	< **130**	< **200**	< **600**
Pr	*RNAA*	NA	*< 4*	*21 ± 4*	*16 ± 4*
Nd	INAA	**24.8** (16.9-29.1)	< **1000**	< **500**	< **1000**
Nd	*RNAA*	NA[c]	*< 20*	< 20	< 2.5
Sm	INAA	**7.5** (4.5-8.6)	**1.5** (1.2-2.1)	**9.1** (5.0-20.1)	**10.8** (5.3-15.3)
Eu	INAA	**1.11** (0.89-1.20)	< **1**	**1.6** (1.0-3.4)	**3.0** (1.2-3.6)
Eu	*RNAA*	NA[c]	*0.7 ± 0.07*	*3.3 ± 0.1*	*3.1 ± 0.2*
Gd	INAA	< 25	< **400**	< **600**	< **1500**
Gd	*RNAA*	NA[c]	*< 15*	< 25	< 25
Tb	INAA	**0.82** (0.49-0.92)	< **1**	< **1**	< 2
Tb	*RNAA*	NA[c]	*< 0.5*	*< 1*	*< 1*
Ho	INAA	**1.33** (0.71-1.59)	< **10**	< **10**	< **20**
Ho	*RNAA*	NA[c]	< 0.4	*3.3 ± 0.4*	*< 0.4*
Tm	INAA	**0.60** (0.37-0.66)	< **10**	< **4**	< **10**
Tm	*RNAA*	NA[c]	< 5	*< 5*	*< 8*
Yb	INAA	**3.46** (1.92-3.88)	< **10**	< **10**	< **20**
Yb	*RNAA*	NA[c]	< 0.5	*6.9 ± 0.6*	*6.0 ± 0.5*
Lu	INAA	**0.49** (0.29-0.55)	< **3**	< **3**	< **6**
Lu	*RNAA*	NA[c]	*< 0.2*	*1.1 ± 0.1*	*0.5 ± 0.1*
Th	INAA	**13.2** (8.0-15.5)	< **5**	**19.0** (10.2-43.1)	**18.0** (7.1-23.8)
U	INAA	**2.8** (1.8-3.2)	**13** (6-17)	< **15**	< 30

Appendix

Table A.4: Results for the lanthanides, Th and U in fruits by INAA and RNAA (in ng.g^{-1}, dry mass) [a,b] (Kurčera et al., 2007)

Element	Method	Apple (N=3)	Apricot (N=3)	Wine grape (N=3)
La	INAA	**26.3** (25.9-46.1)	**19.3** (9.1-55.6)	**42.7** (27.1-176)
Ce	INAA	**31** (24-41)	**37** (14-88)	**127** (41-214)
Pr	INAA	< **150**	< **200**	< **200**
Pr	*RNAA*	NA[c]	< 4	NA[c]
Nd	INAA	< **200**	< **200**	< **500**
Nd	*RNAA*	NA[c]	*< 25*	NA[c]
Sm	INAA	< **0.5**	**1.3** (1.1-3.6)	**1.6** (0.6-2.9)
Sm	*RNAA*	NA[c]	*1.6 ± 0.3*	NA[c]
Eu	INAA	< 0.5	**1.1 (0.5-1.1)**	**7.6** (0.8-14.5)
Eu	*RNAA*	NA[c]	*0.5 ± 0.05*	NA[c]
Gd	INAA	< **100**	< **1000**	< **1200**
Gd	*RNAA*	NA[c]	< **15**	NA[c]
Tb	INAA	< **1**	< **1**	< **1**
Tb	*RNAA*	NA[c]	*< 1*	NA[c]
Ho	INAA	< **10**	< **10**	< **15**
Ho	*RNAA*	NA[c]	*< 4*	NA[c]
Tm	INAA	< **8**	< **10**	< **10**
Tm	*RNAA*	NA[c]	*< 4*	NA[c]
Yb	INAA	< 15	< **12**	< **15**
Yb	*RNAA*	NA[c]	*0.9 ± 0.2*	NA[c]
Lu	INAA	< **2**	< **3**	< **3**
Lu	*RNAA*	NA[c]	< 0.15	NA[c]
Th	INAA	< **3**	**9.3** (6.5-12.1)	**4.1** (< 3-4.1)
U	INAA	< **30**	< **30**	< 40

[a] INAA results are given as median (in bold letters) and range (in brackets), RNAA results are given in italics, and represent results for individual samples ± combined uncertainties.
[b] N: Number of samples from different locations of the polluted region.
[c] Not analyzed.

Table A.5: Results for the lanthanides, Th and U in vegetables by INAA and RNAA (in ng.g^{-1}, dry mass) [a,b] (Kurčera et al., 2007)

Element	Cauliflower (N=3)	Cucumber (N=5)	Kale (N=3)	Parsley root (N=4)	Tomato (N=5)
La	**20.2** (15-27)	**26.0** (12-46.4)	**37.3** (31.3-67.8)	**1025** (475-1795)	**11.1** (4.1-24.2)
Ce	**46** (33-58)	**84** (82-121)	**65** (62-68)	**1822** (815-3262)	**36** (30-45)
Pr	< **150**	< **300**	< **300**	< **750**	< **750**
Pr	< 6	9.3 ± *2.5*	*17.2 ± 3.5*	586 ± 30	*17.2 ± 3.5*
Nd	< **250**	< **500**	< **350**	**820** (408-1666)	< **350**
Nd	< **25**	*< 40*	< **40**	*1276 ± 42*	*< 30*
Sm	**5.8** (0.5-25.2)	**4.4** (1.0-8.0)	**5.3** (0.6-15.3)	**155.3** (76.6-306.9)	**3.1** (3.0-4.3)
Sm	2.4 ± *0.05*	*7.8 ± 0.08*	14.5 ± 0.3	*514.3 ± 10.1*	*4.2 ± 0.6*
Eu	**0.7** (0.5-0.8)	**0.8 (0.5-3.9)**	**1.0** (0.5-1.5)	**28.2** (13.2-57.5)	**0.5** (0.4-0.6)
Eu	0.6 ± *0.04*	*0.9 ± 0.06*	0.8 ± 0.05	*45.2 ± 3.7*	*0.4 ± 0.06*
Gd	< **2500**	< **2000**	< **2500**	< **2500**	< **2700**
Gd	< *16*	< **25**	< *30*	*520 ± 70*	< *20*
Tb	< **2**	< **2**	< **2**	**20** (10-36)	< **2**
Tb	< **1.5**	< *1.5*	< *2*	*34.2 ± 3.7*	< **2.0**
Ho	< 15 (<15-68)	<**10**	< **20**	< **20** (< 20-165.5)	< **10**
Ho	< **0.5**	2.3 ± *0.3*	3.9 ± 0.04	117 ± *1.2*	*0.8 ± 0.2*
Tm	< 15	< **10**	< **15**	< **35**	< **15**
Tm	< 6	< *8*	< *10*	*27.5 ± 1.2*	< *7*
Yb	< 15	< **12**	< **15**	57 (25-129)	< **15**
Yb	< 0.7	*1.5 ± 0.3*	8.0 ± 0.08	*28.8 ± 1.2*	*1.1 ± 0.3*
Lu	< 4	< **3**	< **4**	**15.8** (9.8-22.9)	< **4**
Lu	3 ± 0.08	0.5 ± *0.1*	1.5 ± 0.2	*22.6 ± 0.08*	*0.6 ± 0.07*
Th	< **6**	**9.8** (8.9-10.2)	**14.2** (12.8-15.7)	**274** (157-600)	< **5**
U	< 50	< **30**	< **50**	120 (< 50-133)	< **50**

Appendix

Table B.1: Influence of graded REE applications on mean of soil pH (1:2.5) and soil electro-chemical conductivity (EC, in mS m^{-1}) of maize and oilseed rape 66 days after sowing (2005)

Application rate ($\mu g\ g^{-1}$)	Soil pH			Soil Electrochemical conductivity (mS m^{-1})		
	Maize	**Oilseed rape**	**Non-vegetated soil**	**Maize**	**Oilseed rape**	**Non-vegetated soil**
Lanthanum						
0	5.1 a	5.4 a	6.2 b	130.0 a	154.0 a	402.3 a
1.0	5.3 a	5.3 a	6.2 b	129.8 a	112.3 a	386.5 a
10	5.3 a	5.4 a	6.2 b	150.8 a	138.3 a	410.0 a
50	5.3 a	5.5 a	6.1 ab	113.0 a	142.8 a	414.3 a
100	5.3 a	5.4 a	5.9 a	133.8 a	140.8 a	403.5 a
Cerium						
0	5.1 a	5.4 a	6.2 a	130.0 a	154.0 a	402.3 a
0.8	5.7 b	5.3 a	6.1 a	141.0 a	124.3 a	395.0 a
8.0	5.4 ab	5.2 a	5.9 a	170.5 a	128.3 a	381.5 a
40	5.4 ab	5.4 a	5.9 a	116.3 a	117.0 a	381.5 a
80	5.3 ab	5.6 a	6.2 a	121.5 a	128.5 a	400.0 a
REE-fertilizer						
0	5.1 a	5.4 a	6.2 b	130.0 a	154.0 a	402.3 a
2.7	5.9 ab	5.4 a	5.4 a	122.5 a	137.8 a	407.5 a
27	6.1 b	5.5 a	5.6 ab	160.8 a	138.5 a	395.0 a
135	6.1 ab	5.5 a	5.4 ab	154.8 a	141.8 a	380.0 a
270	6.0 b	5.5 a	5.6 a	163.5 a	195.3 a	404.8 a
Calcium						
0	5.1 a	5.4 a	6.2 a	130.0 a	154.0 a	402.3 a
9.83	6.2 ab	5.6 ab	5.2 a	152.0 a	125.3 a	389.8 a
98.3	6.2 bc	5.6 ab	5.4 a	191.5 a	150.8 a	386.5 a
491.5	6.2 c	5.6 ab	5.6 a	310.3 b	277.0 b	427.3 a
983	6.2 d	5.7 b	5.9 a	365.8 b	401.5 b	496.0 b
Copper						
0	5.1 a	5.4 a	6.2 c	130.0 ab	154.0 a	402.3 a
4.3	6.1 a	5.7 a	5.4 bc	138.0 ab	149.8 a	380.5 a
43	6.1 a	5.7 a	5.4 bc	114.7 a	171.8 ab	378.3 a
215	5.9 a	5.6 a	5.6 b	235.8 bc	234.0 b	393.8 a
430	5.8 a	5.3 a	5.5 a	264.0 c	213.8 ab	373.0 a

Table B.2: Influence of graded REE applications on mean of soil microbial counts (CFU) of maize and oilseed rape 66 days after sowing (2006)

Application rate ($\mu g\ g^{-1}$)	Maize			Oilseed rape		
	Heterotrophic bacteria	**Actino-mycetes**	**Fungi**	**Heterotrophic bacteria**	**Actino-mycetes**	**Fungi**
Lanthanum						
0	5.5×10^6 a	9.7×10^5 a	2.8×10^6 b	4.9×10^6 a	3.5×10^6 a	3.5×10^6 a
1.0	2.7×10^7 b	1.3×10^6 ab	2.1×10^6 ab	3.2×10^7 c	1.8×10^6 a	8.8×10^6 a
10	2.8×10^7 b	2.1×10^6 bc	2.1×10^6 ab	1.9×10^7 bc	2.1×10^6 a	5.9×10^6 a
50	4.0×10^7 b	2.5×10^6 c	2.2×10^6 ab	1.9×10^7 bc	3.9×10^6 a	3.9×10^6 a
100	4.0×10^7 b	1.6×10^6 abc	1.8×10^6 a	1.5×10^7 ab	5.5×10^6 a	5.3×10^6 a
Cerium						
0	5.5×10^6 a	9.7×10^5 a	2.8×10^6 a	4.9×10^6 b	3.5×10^6 a	3.5×10^6 a
0.8	2.9×10^7 b	2.2×10^6 b	2.2×10^6 a	3.4×10^6 a	2.2×10^6 a	3.1×10^6 a
8.0	3.2×10^7 b	1.4×10^6 ab	2.3×10^6 a	3.5×10^6 a	1.5×10^6 a	6.4×10^6 ab
40	4.3×10^7 b	1.8×10^6 ab	2.1×10^6 a	3.7×10^6 a	2.2×10^6 a	4.7×10^6 a
80	3.1×10^7 b	1.1×10^6 a	1.9×10^6 a	3.7×10^6 a	1.9×10^6 a	1.1×10^7 b
REE-fertilizer						
0	5.5×10^6 a	9.7×10^5 a	2.8×10^6 a	4.9×10^6 b	3.5×10^6 a	3.5×10^6 a
2.7	3.8×10^7 b	2.9×10^6 ab	2.8×10^6 a	3.8×10^6 a	5.9×10^6 a	4.4×10^6 ab
27	3.1×10^7 b	6.7×10^6 b	3.6×10^6 a	3.7×10^6 a	2.1×10^6 a	4.8×10^6 ab
135	3.8×10^7 b	3.4×10^6 ab	3.7×10^6 a	3.8×10^6 a	1.8×10^6 a	8.9×10^6 b
270	3.6×10^7 b	3.0×10^6 ab	2.8×10^6 a	3.2×10^6 a	2.1×10^6 a	2.7×10^6 a
Calcium						
0	5.5×10^6 a	9.7×10^5 a	2.8×10^6 a	4.9×10^6 b	3.5×10^6 a	3.5×10^6 a
1.0	3.9×10^7 b	1.1×10^6 ab	2.1×10^6 a	3.7×10^6 a	2.3×10^6 a	8.2×10^6 a
10	3.9×10^7 b	1.5×10^6 ab	1.9×10^6 a	3.6×10^6 a	2.3×10^6 a	7.3×10^6 a
50	4.5×10^7 b	8.8×10^6 b	2.2×10^6 a	3.7×10^6 a	3.0×10^6 a	3.4×10^6 a
100	4.3×10^7 b	6.1×10^6 ab	2.5×10^6 a	3.9×10^6 ab	4.2×10^6 a	5.4×10^6 a

Appendix

Table B.3: Influence of graded REE applications on some soil enzyme activities (mean) of maize and oilseed rape 66 days after sowing (2005)

Application rate (µg g^{-1})	Dehydrogenase activity (TPF)			Alkaline phosphatase activity (p-NP)		
	Maize	**Oilseed rape**	**Non-vegetated soil**	**Maize**	**Oilseed rape**	**Non-vegetated soil**
Lanthanum						
0	16.6 a	19.5 a	3.1 a	72.2 a	133.8 b	185.3 a
1.0	18.2 a	19.2 a	3.4 a	81.1 a	52.4 a	189.8 a
10	15.3 a	19.5 a	3.8 a	128.1 a	101.1 ab	204.7 a
50	18.9 a	21.7 a	2.9 a	100.0 a	116.2 b	210.9 a
100	17.7 a	19.1 a	2.2 a	120.7 a	91.5 ab	197.6 a
Cerium						
0	16.6 a	19.5 ab	3.1 a	72.2 a	133.8 a	185.3 ab
0.8	16.7 a	20.0 ab	3.2 a	106.0 a	92.1 a	152.4 ab
8.0	13.3 a	17.9 a	3.4 a	97.7 a	127.3 a	141.5 a
40	15.5 a	21.0 ab	2.9 a	106.8 a	105.7 a	192.6 b
80	15.3 a	23.2 b	3.0 a	70.9 a	108.8 a	201.3 b
REE-fertilizer						
0	16.6 bc	19.5 a	3.1 a	72.2 a	133.8 b	185.3 a
2.7	18.0 c	21.8 a	3.4 a	62.6 a	92.3 ab	136.5 a
27	13.7 ab	21.0 a	3.8 a	70.2 a	99.9 ab	126.4 a
135	12.8 a	22.0 a	2.9 a	55.1 a	130.6 b	184.0 a
270	12.3 a	14.2 a	2.2 a	63.9 a	86.2 a	131.9 a
Calcium						
0	16.6 b	19.5 bc	3.1 ab	72.2 a	133.8 a	185.3 a
9.83	12.9 ab	24.7 c	2.8 ab	73.5 a	98.9 a	117.5 a
98.3	14.3 ab	20.5 c	3.8 ab	95.8 a	88.8 a	156.8 a
491.5	9.4 a	13.5 ac	2.5 a	72.1 a	140.5 a	187.5 a
983	13.3 ab	11.4 a	4.3 b	174.1 b	72.5 a	120.0 a
Copper						
0	16.6 b	19.5 c	3.1 bc	72.2 ab	133.8 a	185.3 c
4.3	14.2 b	18.1 c	3.8 c	104.4 b	178.3 a	152.4 c
43	11.2 b	9.6 b	2.6 bc	55.6 a	61.4 a	95.7 b
215	2.1 a	1.5 a	0.8 ab	44.5 a	77.1 a	71.5 ab
430	1.0 a	0.4 a	0.3 a	35.8 a	124.3 a	25.8 a

Appendix

Table B.4: Influence of graded REE applications on mean of biomass production (g pot^{-1}) of maize and oilseed rape 66 days after sowing (2005)

Application rate ($\mu g\ g^{-1}$)	**Maize**			**Oilseed rape**		
	Roots	**Shoots**	**Total**	**Roots**	**Shoots**	**Total**
Lanthanum						
0	3.9a	11.6 a	15.5 a	1.0 a	9.0 a	10.0 a
1.0	2.8a	10.7 a	13.5 a	1.9 a	16.9 a	18.9 a
10	1.2a	4.2 a	5.4 a	2.1 a	15.5 a	17.6 a
50	3.5a	14.8 a	18.4 a	2.4 a	18.2 a	20.5 a
100	3.9a	13.6 a	17.2 a	1.0 a	11.6 a	12.7 a
Cerium						
0	3.9a	11.6 a	15.5 a	1.0 a	9.0 a	10.0 a
0.8	1.7a	6.2 a	7.9 a	2.5 a	17.1 ab	19.5 a
8.0	2.1a	7.0 a	9.2 a	1.3 a	32.4 b	33.8 a
40	4.4a	16.8 a	21.2 a	1.6 a	13.4 ab	15.0 a
80	4.0a	11.9 a	15.9 a	2.0 a	18.3 ab	20.4 a
REE fertilizer						
0	3.9a	11.6 a	15.5 a	1.0 ab	9.0 ab	10.0 ab
2.7	6.8b	18.2 a	24.9 a	1.8 ab	18.5 b	20.3 b
27	1.4ab	3.7 a	5.1 a	2.8 b	18.2 b	20.9 b
135	2.7ab	7.2 a	9.8 a	2.4 ab	17.3 b	19.7 b
270	4.5ab	13.4 a	17.9 a	0.4 a	3.6 a	4.0 a
Calcium						
0	3.9	11.6	15.5	1.0	9.0	10.0
9.83	3.9	10.7	14.7	2.6	18.5	21.1
98.3	2.2	5.3	7.5	0.9	10.2	11.1
491.5	do	do	do	do	do	do
983	do	do	do	do	do	do
Copper						
0	3.9	11.6	15.5	1.0	9.0	10.0
4.3	5.9	15.5	21.3	1.2	8.4	9.6
43	3.9	10.8	14.6	do	do	do
215	do	do	do	do	do	do
430	do	do	do	do	do	do

Appendix

Table B.5: Influence of graded REE applications on mean of germination rate and plant height of maize and oilseed rape 66 days after sowing (2005)

Application rate ($\mu g\ g^{-1}$)	**Maize**		**Oilseed rape**	
	Germination rate (%)	**Plant height (cm)**	**Germination rate (%)**	**Plant height (cm)**
Lanthanum				
0	91.6 a	66.7 a	67.5 a	24.5 a
1.0	91.6 a	68.2 a	57.5 a	29.5 a
10	87.5 a	35.2 a	62.5 a	31.5 a
50	91.6 a	73.7 a	77.5 a	30.2 a
100	95.8 a	72.7 a	62.5 a	22.0 a
Cerium				
0	91.6 a	66.7 a	67.5 a	24.5 a
0.8	91.6 a	59.2 a	62.5 a	27.0 a
8.0	95.8 a	48.2 a	50.0 a	26.0 a
40	87.5 a	75.7 a	65.0 a	31.2 a
80	95.8 a	70.7 a	75.0 a	28.0 a
REE fertilizer				
0	91.6 a	66.7 a	67.5 b	24.5 a
2.7	91.6 a	66.7 a	55.0 b	24.0 a
27	83.3 a	67.7 a	72.5 b	26.7 a
135	95.8 a	67.0 a	77.5 b	25.2 a
270	87.5 a	70.7 a	15.0 a	21.6 a
Calcium				
0	91.6 c	66.7 b	67.5 b	24.5 b
9.83	87.5 ab	59.3 ab	55.0 bc	24.0 b
98.3	91.6 b	66.6 b	52.5 bc	21.7 ab
491.5	62.5 a	do	22.5 ab	13.6 a
983	16.6 a	do	0.0 a	do
Copper				
0	91.6 c	66.7 a	67.5 c	24.5a
4.3	87.5 c	65.3 a	57.5 bc	24.7a
43	91.6 c	65.0 a	42.5 c	21.6a
215	54.1 b	do	5.0 a	do
430	12.5 a	do	0.0 a	do

do, all plants died off

Values followed by the same letters are not significantly different by Tukey’s test at 0.05 level

Table B.6: Influence of graded REE applications on mean of REE concentration in **shoots** (µg g^{-1}) of maize and oilseed rape 66 days after sowing (2005)

Application rate	Maize				Oilseed rape			
(µg g^{-1})	La	Ce	Pr	Nd	La	Ce	Pr	Nd
Lanthanum								
0	0.032 a	0.045 a	<0.024*	<0.024	0.057 a	0.067 a	<0.024	0.030 a
1.0	0.041 a	0.042 a	<0.024	<0.024	0.067 a	0.063 a	<0.024	0.033 a
10	0.069 a	0.034 a	<0.024	<0.024	0.158 a	0.077 a	<0.024	0.034 a
50	0.234 b	0.039 a	<0.024	<0.024	0.779 ab	0.079 a	<0.024	0.034 a
100	0.685 c	0.042 a	<0.024	<0.024	1.589 a	0.076 a	<0.024	0.031 a
Cerium								
0	0.032 a	0.045 a	<0.024	<0.024	0.057 a	0.067 a	<0.024	0.030 a
0.8	0.036 a	0.044 a	<0.024	<0.024	0.084 a	0.098 a	<0.024	0.036 a
8.0	0.033 a	0.067 a	<0.024	<0.024	0.062 a	0.120 a	<0.024	0.035 a
40	0.031 a	0.149 a	<0.024	<0.024	0.071 a	0.333 b	<0.024	0.035 a
80	0.026 a	0.355 b	<0.024	<0.024	0.067 a	1.112 b	<0.024	0.028 a
REE fertilizer								
0	0.032 a	0.045 a	<0.024	<0.024 a	0.057 a	0.067 a	<0.024	0.030 a
2.7	0.045 a	0.059 a	0.054	0.025 a	0.072 a	0.107 a	<0.024	0.047 a
27	0.093 a	0.109 a	0.076	0.039 a	0.181 a	0.209 a	0.025	0.032 a
135	0.415 b	0.453 b	<0.024	0.147 b	0.608 a	0.674 ab	0.067	0.060 ab
270	0.816 c	0.791 b	<0.024	0.252 b	1.586 b	1.468 b	0.146	0.211 b
Calcium								
0	0.032	0.045	<0.024	<0.024	0.057	0.067	<0.024	0.030
9.83	0.028	0.044	0.063	0.024	0.062	0.117	<0.024	0.033
98.3	0.197	0.322	<0.024	0.111	0.057	0.090	<0.024	0.029
491.3	< 0.02	<0.024	<0.024	<0.024	0.069	0.113	<0.024	<0.024
983	do	do	do	do	do	do	do	do
Copper								
0	0.032	0.045	<0.024	<0.024	0.057	0.067	<0.024	0.030
4.3	0.027	0.033	<0.024	0.046	0.077	0.103	0.031	0.488
43	0.037	0.050	<0.024	<0.024	0.101	0.136	<0.024	0.035
215	0.064	0.110	<0.024	<0.024	do	do	do	do
430	do	do	do	do	do	do	do	do

*< lower limit of quantitation do, all plants died off

Appendix

Table B.7: Influence of graded REE applications on mean of REE concentration in **roots** (µg g^{-1}) of maize and oilseed rape 66 days after sowing (2005)

Application rate (µg g^{-1})	Maize				Oilseed rape			
	La	**Ce**	**Pr**	**Nd**	**La**	**Ce**	**Pr**	**Nd**
Lanthanum								
0	1.97 a	3.90 a	0.419 a	1.486 a	1.64 a	3.12 a	0.306 a	1.067 a
1.0	1.97 a	3.29 a	0.345 a	1.208 a	2.10 a	3.32 a	0.323 a	1.129 a
10	4.30 a	4.03 a	0.426 a	1.516 a	4.94 a	2.87 a	0.282 a	0.983 a
50	10.17 b	3.35 a	0.349 a	1.227 a	16.84 b	2.83 a	0.271 a	0.952 a
100	29.65 c	3.44 a	0.342 a	1.174 a	54.60 c	3.74 a	0.359 a	1.253 a
Cerium								
0	1.97 a	3.90 a	0.419 a	1.486 a	1.64 a	3.12 a	0.306 a	1.067 a
0.8	2.00 a	4.07 a	0.393 a	1.363 a	2.49 a	3.79 a	0.349 a	1.205 a
8.0	3.10 a	9.17 a	0.628 a	2.205 a	1.99 a	5.59 a	0.374 a	1.315 a
40	2.47 a	11.50 a	0.523 a	1.833 a	1.56 a	9.87 a	0.291 a	1.049 a
80	2.66 a	32.16 b	0.564 a	1.959 a	2.01 a	38.69 b	0.365 a	1.294 a
REE fertilizer								
0	1.97 a	3.90 a	0.419 a	1.486 a	1.64 a	3.12 a	0.306 a	1.067 a
2.7	4.15 a	8.31 a	0.856 a	3.051 a	2.83 a	5.23 a	0.514 a	1.764 a
27	7.91 a	14.66 a	1.512 a	5.107 a	4.69 a	7.95 a	0.787 a	2.584 a
135	25.73 b	41.65 b	4.242 b	13.681 b	19.95 a	30.25 a	3.019 a	9.761 a
270	50.30 c	76.23 c	7.554 c	24.126 c	110.66 b	136.54 b	12.927 b	41.457 b
Calcium								
0	1.97	0.90	0.419	1.486	1.64	3.12	0.306	1.067
9.83	2.46	5.28	0.516	1.808	1.83	3.61	0.340	1.183
98.3	2.03	4.17	0.429	1.510	1.49	2.75	0.265	0.923
491.3	do	do	do	do	do	2.75	0.276	0.985
983	do	do	do	do	do	do	do	do
Copper								
0	1.97	3.90	0.419	1.486	1.64	3.12	0.306	1.067
4.3	2.67	5.45	0.558	1.962	2.36	4.57	0.455	1.596
43	2.55	5.28	0.539	1.908	1.99	3.99	3.860	1.356
215	do	do	do	do	do	do	do	do
430	do	do	do	do	do	do	do	do

do, all plants died off
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Appendix

Table B.8: Influence of graded REE applications on mean of REE uptake (µg pot^{-1}) by maize 66 days after sowing (2005)

Application rate (µg g^{-1})	**Uptake by maize roots (µg pot^{-1})**				**Uptake by maize shoots (µg pot^{-1})**			
	La	**Ce**	**Pr**	**Nd**	**La**	**Ce**	**Pr**	**Nd**
Lanthanum								
0	7.1 a	14.0 a	1.5 a	5.3 a	0.4 a	0.5 a	----*	----*
1.0	5.4 a	8.8 a	0.9 a	3.2 a	0.5 a	0.4 a	----*	----*
10	5.2 a	4.9 a	0.5 a	1.8 a	0.3 a	0.2 a	----*	-----*
50	39.3 a	11.6 a	1.2 a	4.2 a	3.9 a	0.6 a	-----*	-----*
100	119.2 b	14.5 a	1.5 a	5.0 a	9.4 b	0.7 a	-----*	-----*
Cerium								
0	7.1 a	14.0 a	1.5 a	5.3 a	0.4 a	0.5 a	----*	----*
0.8	3.2 a	6.0 a	0.6 a	2.0 a	0.2 a	0.3 a	----*	----*
8.0	3.8 a	11.6 a	0.8 a	2.7 a	0.2 a	0.5 a	----*	----*
40	10.4 a	51.0 ab	2.2 a	7.7 a	0.6 a	3.0 ab	-----*	----*
80	11.6 a	139.4 b	2.5 a	8.5 a	0.3 a	4.4 b	-----*	----*
REE fertilizer								
0	7.1 a	14.0 a	1.5 a	5.3a	0.4 a	0.5 a	----	0.2 a
2.7	27.8 a	55.6 a	5.7 a	20.4 a	0.8 a	1.1 a	-----	0.4 a
27	10.3 a	19.2 a	2.0 a	6.7 a	0.3 a	0.4 a	-----	0.1 a
135	56.6 a	94.6 a	9.7 a	31.1 a	2.1 a	2.2 a	0.2	0.7 a
270	243.4 b	367.6 b	36.4 b	116.0 b	11.4 b	11.1 b	1.1	3.5 b
Calcium								
0	7.1	14.0	1.5	5.3	0.4	0.5	----*	0.2
9.83	8.9	19.8	1.9	6.6	0.2	0.4	----*	0.1
98.3	4.8	9.9	1.0	3.6	0.1	0.3	----*	----*
491.3	do	do	do	do	do	do	do	do
983	do	do	do	do	do	do	do	do
Copper								
0	7.1	14.0	1.5	5.3	0.4	0.5	-----*	----*
4.3	16.2	32.9	3.4	11.9	0.4	0.5	-----*	----*
43	10.5	20.9	2.2	7.7	0.4	0.5	-----*	----*
215	do	do	do	do	do	do	do	do
430	do	do	do	do	do	do	do	do

* < lower limit of quantitation do, all plants died off

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Appendix

Table B.9: Influence of graded REE applications on mean of REE uptake (µg pot^{-1}) by oilseed rape 66 days after sowing (2005)

Application rate (µg g^{-1})	Uptake by oilseed rape roots (µg pot^{-1})				Uptake by oilseed rape shoots (µg pot^{-1})			
	La	Ce	Pr	Nd	La	Ce	Pr	Nd
Lanthanum								
0	1.7 a	3.3 a	0.3 a	1.1 a	0.5 a	0.6 a	-----*	0.3 a
1.0	3.9 ab	6.2 a	0.6 a	2.1 a	1.1 a	1.1 a	----*	0.6 a
10	11.3 ab	7.0 a	0.7 a	2.4 a	2.6 a	1.2 a	-----*	0.5 a
50	38.6 ab	6.8 a	0.7 a	2.3 a	10.5 ab	1.0 a	-----*	0.4 a
100	58.3 b	4.8 a	0.5 a	1.6 a	19.1 b	0.9 a	-----*	0.4 a
Cerium								
0	1.7 a	3.3 a	0.3 a	1.1 a	0.5 a	0.6 a	-----*	0.3 a
0.8	6.8 a	9.7 a	0.9 a	3.2 a	1.4 a	1.6 a	------*	0.6 a
8.0	2.6 a	7.4 a	0.5 a	1.7 a	2.2 a	4.4 a	-----*	1.5 b
40	2.5 a	15.5 a	0.5 a	1.6 a	0.9 a	4.2 a	-----*	0.5 a
80	4.5 a	73.4 b	0.8 a	2.9 a	1.2 a	19.8b	------*	0.5 a
REE fertilizer								
0	1.7 a	3.3 a	0.3 a	1.1 a	0.5 a	0.6 a	-----*	0.3 a
2.7	5.3 a	9.9 ab	1.0 ab	3.4 ab	1.4 a	2.0 a	----*	0.6 a
27	13.3 ab	22.4 ab	2.2 ab	7.3 ab	3.2 a	3.7 a	0.4	1.1 a
135	50.1 b	75.9 c	7.6 c	17.0 c	11.2 b	12.4 b	1.2	3.9 b
270	45.9 b	56.1 bc	5.3 bc	10.3 bc	8.0 a	7.2 ab	0.7	2.4 ab
Calcium								
0	1.7 ab	3.3 ab	0.3 ab	1.1 ab	0.5 ab	0.6 a	-----*	0.3 ab
9.83	4.6 b	9.1 b	0.8 b	2.9 b	1.1 b	2.2 b	-----*	0.6 b
98.3	1.4 ab	2.6 ab	0.2 ab	0.9 ab	0.6 ab	0.9 ab	-----*	0.2 ab
491.3	0.6 a	1.2 a	0.1 a	0.4 a	0.1 a	0.2 a	-----*	0.1 a
983	do	do	do	do	do	Do	do	do
Copper								
0	1.7	3.3	0.3	1.1	0.5	0.6	-----*	0.3
4.3	2.9	5.7	0.6	1.9	0.6	0.8	-----*	0.3
43	0.2	0.5	0.1	0.2	0.3	0.3	-----*	0.1
215	do	do	do	do	do	do	do	do
430	do	do	do	do	do	do	do	do

* < lower limit of quantitation do, all plants died off

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Appendix

Table B.10: Influence of graded REE applications on mean of REE concentration in shoots (µg g^{-1}) of maize and oilseed rape 35 days after sowing (2006)

Application rate	Maize				Oilseed rape			
(µg g^{-1})	La	Ce	Pr	Nd	La	Ce	Pr	Nd
Lanthanum								
0	0.09 a	0.16 a	<0.03*	0.06 a	0.06 a	0.56 a	0.05 a	0.17 a
1.0	0.10 a	0.11 a	<0.03	0.04 a	0.50 a	0.59 a	0.06 a	0.18 a
10	0.41 a	0.11 a	<0.03	0.04 a	0.89 a	0.36 a	0.04 a	0.12 a
50	1.63 b	0.16 a	<0.03	0.06 a	3.84 a	0.51 a	0.05 a	0.16 a
100	2.64 c	0.11 a	<0.03	0.04 a	14.67 b	0.49 a	0.05 a	0.15 a
Cerium								
0	0.09 a	0.16 a	<0.03	0.06 a	0.06 a	0.56 a	0.05 a	0.17 a
0.8	0.42 a	0.13 a	<0.03	0.04 a	1.39 b	0.52 a	0.04 a	0.13 a
8.0	0.37 a	0.41 ab	<0.03	0.05 a	0.64 ab	1.08 a	0.04 a	0.11 a
40	0.28 a	0.82 b	<0.03	0.08 a	0.53 a	2.87 ab	0.05 a	0.17 a
80	0.11 a	1.40 c	<0.03	0.04 a	0.30 a	4.70 b	0.03 a	0.09 a
REE-fertilizer								
0	0.09 a	0.16 a	<0.03	0.06 a	0.06 a	0.56 a	0.05 a	0.17 a
2.7	0.09 a	0.15 a	<0.03	0.05 a	0.38 a	0.49 a	0.04 a	0.14 a
27	0.39 ab	0.67 a	0.07	0.22 a	1.11 a	1.74 a	0.17 a	0.51 a
135	1.29 b	1.84 b	0.19	0.59 b	3.13 a	4.94 a	0.49 a	1.51 a
270	3.36 c	3.66 c	0.37	1.24 c	7.65 b	13.45 b	1.39 b	4.18 b
Calcium								
0	0.09 a	0.16 a	<0.03	0.06 a	0.06	0.56	0.05	0.17
1.0	0.11 a	0.39 b	<0.03	0.04 a	0.23	0.65	<0.03	0.07
10	0.10 a	0.21 ab	<0.03	0.04 a	---**	----**	----**	-----**
50	0.07 a	0.14 a	<0.03	0.04 a	0.43	0.81	0.07	0.23
100	0.08 a	0.14 a	<0.03	0.05 a	0.26	0.38	0.03	0.11

* < lower limit of quantitation ** no data

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Table B.11: Influence of graded REE applications on mean of REE concentration in roots (µg g^{-1}) of maize and oilseed rape 35 days after sowing (2006)

Application	Maize				Oilseed rape			
rate (mg kg^{-1})	La	Ce	Pr	Nd	La	Ce	Pr	Nd
Lanthanum								
0	1.32 a	2.16 a	0.21 a	0.74 a	1.89 a	2.56 a	0.25 a	0.71 a
1.0	2.68 a	3.67 b	3.67 b	1.12 a	2.81 a	2.87 a	0.27 a	0.82 a
10	10.57 a	2.99 ab	2.99 ab	0.96 a	4.51 a	1.39 a	0.09 a	0.31 a
50	33.63 a	3.19 ab	3.19 ab	0.99 a	22.07 a	1.38 a	0.12 a	0.39 a
100	238.65 b	2.69 ab	2.96 ab	0.88 a	120.50 b	3.73 a	0.34 a	1.00 a
Cerium								
0	1.32 a	2.16 a	0.21 a	0.74 a	1.89 a	2.56 a	0.25 a	0.71 a
0.8	2.64 a	3.42 a	0.26 a	0.93 a	6.31 a	5.30 a	0.52 a	1.51 a
8.0	2.07 a	10.68 a	0.35 a	0.93 a	1.13 a	5.35 a	0.14 a	0.43 a
40	1.81 a	24.05 a	0.30 a	1.19 a	1.33 a	16.08 b	0.15 a	0.50 a
80	1.59 a	26.29 b	0.23 a	0.79 a	1.14 a	33.09 c	0.13 a	0.37 a
REE-fertilizer								
0	1.32 a	2.16 a	0.21 a	0.74 a	1.89 a	2.56 a	0.25 a	0.71 a
2.7	2.30 a	4.13 a	0.39 a	1.35 a	2.00 a	2.71 a	0.25 a	0.82 a
27	6.26 a	10.97 a	1.08 a	3.57 a	5.01 a	7.79 a	0.73 a	2.36 a
135	48.29 a	63.74 a	6.06 a	19.70 a	15.83 a	21.92 a	2.07 a	6.72 a
270	342.31 b	434.38 b	40.95 b	131.43 b	106.85 b	136.43 b	12.73 b	40.26 b
Calcium								
0	1.32 a	2.16 a	0.21 a	0.74 a	1.89 a	2.56 a	0.25 a	0.71 a
1.0	2.39 a	4.55 b	0.37 a	1.25 a	1.17 a	1.79 a	0.12 a	0.42 a
10	1.65 a	3.16 ab	0.26 a	0.90 a	1.44 a	2.40 a	0.20 a	0.67 a
50	2.01 a	3.79 ab	0.34 a	1.18 a	1.99 a	2.20 a	0.20 a	0.65 a
100	1.29 a	2.77 ab	0.25 a	0.89 a	2.08 a	2.95 a	0.26 a	0.85 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Appendix

Table B.12: Influence of graded REE applications on mean of REE concentration in **shoots** ($\mu g\ g^{-1}$) of maize and oilseed rape 66 days after sowing (2006)

Application rate	**Maize**				**Oilseed rape**			
($\mu g\ g^{-1}$)	**La**	**Ce**	**Pr**	**Nd**	**La**	**Ce**	**Pr**	**Nd**
Lanthanum								
0	0.09	0.23	<0.05*	<0.05	0.23 a	0.38 a	<0.05	0.13 a
1.0	0.07	0.09	<0.05	<0.06	0.25 a	0.31 a	<0.05	0.10 a
10	0.16	0.16	<0.06	0.07	0.96 a	0.43 a	0.07	0.15 a
50	----**	-------**	------**	------**	3.94 ab	0.56 a	0.11	0.21 a
100	0.99	0.13	<0.05	<0.05	6.69 b	0.67 a	0.09	0.22 a
Cerium								
0	0.09	0.23	<0.05	<0.05	0.23 a	0.38 a	<0.05	0.13 a
0.8	0.09	0.17	<0.05	0.07	0.25 a	0.36 a	<0.05	0.13 a
8.0	0.06	0.21	<0.05	0.06	0.18 a	0.66 a	<0.05	0.09 a
40	0.06	0.29	<0.05	0.07	0.18 a	2.03 b	<0.05	0.11 a
80	0.06	0.55	<0.05	0.05	0.19 a	3.38 c	<0.05	0.10 a
REE-fertilizer								
0	0.09 a	0.23 a	<0.05	<0.05	0.23 a	0.38 a	<0.05	0.13 a
2.7	0.06 a	0.09 a	<0.05	0.07	0.23 a	0.36 a	0.07	0.12 a
27	0.15 a	0.24 a	<0.05	0.08	0.79 a	1.13 a	0.12	0.35 a
135	0.43 a	0.51 a	0.07	0.16	2.47 b	3.75 b	0.41	1.36 b
270	1.68 b	1.79 b	0.18	0.58	3.74 c	5.66 c	0.61	2.01 c
Calcium								
0	0.09	0.23	<0.05	<0.05	0.23 a	0.38 a	<0.05	0.13 a
1.0	0.08	0.10	<0.05	<0.05	0.14 a	0.19 a	<0.05	0.07 a
10	0.09	0.12	<0.05	0.09	0.15 a	0.24 a	<0.05	0.08 a
50	0.05	0.07	<0.05	<0.05	0.13 a	0.22 a	<0.05	0.08 a
100	0.08	0.09	<0.05	0.06	0.13 a	0.21 a	<0.05	0.08 a

*< lower limit of quantitation ** no data

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Table B.13: Influence of graded REE applications on mean of REE concentration in **roots** ($\mu g\ g^{-1}$) of maize and oilseed rape 66 days after sowing (2006)

Application	**Maize**				**Oilseed rape**			
rate ($\mu g\ g^{-1}$)	**La**	**Ce**	**Pr**	**Nd**	**La**	**Ce**	**Pr**	**Nd**
Lanthanum								
0	4.24 a	8.84 a	0.89 a	3.28 a	9.54 a	19.14 a	1.89 a	6.78 a
1.0	4.04 a	7.93 a	0.81 a	2.92 a	11.74 a	20.58 a	2.07 a	7.44 a
10	8.97 a	8.35 a	0.86 a	3.12 a	23.46 a	17.89 a	1.77 a	6.37 a
50	21.31 b	7.63 a	0.77 a	2.83 a	75.44 b	18.00 a	1.72 a	6.13 a
100	54.64 c	9.12 a	0.92 a	3.35 a	126.21 c	18.21 a	1.79 a	6.36 a
Cerium								
0	4.24 a	8.84 a	0.89 a	3.28 a	9.54 a	19.14 a	1.89 a	6.78 a
0.8	3.97 a	8.81 a	0.87 a	3.16 a	8.49 a	18.31 a	1.68 a	6.09 a
8.0	3.84 a	12.89 ab	0.86 a	3.12 a	8.72 a	25.86 a	1.69 a	6.13 a
40	4.44 a	28.27 b	1.00 a	3.61 a	9.25 a	64.01 b	1.85 a	6.52 a
80	4.24 a	51.24 c	0.95 a	3.39 a	9.27 a	118.05 c	1.87 a	6.04 a
REE-fertilizer								
0	4.24 a	8.84 a	0.89 a	3.28 a	9.54 a	19.14 a	1.89 a	6.78 a
2.7	4.73 a	9.83 a	1.02 a	3.64 a	11.21 a	20.99 a	2.10 a	7.35 a
27	10.09 a	19.69 a	2.01 a	6.82 a	29.86 a	50.52 a	5.06 a	16.36 a
135	33.99 a	58.09 a	5.84 a	18.92 a	104.03 b	161.60 b	15.67 b	48.59 b
270	120.63 b	180.34 b	17.89 b	56.71 b	163.49 c	235.55 c	21.92 c	67.23 c
Calcium								
0	4.24 ab	8.84 ab	0.89 ab	3.28 ab	9.54 a	19.14 a	1.89 a	6.78 a
1.0	4.01 a	8.61 a	0.88 a	3.19 a	8.41 a	16.78 a	1.69 a	6.14 a
10	4.66 ab	9.80 ab	1.02 ab	3.72 ab	7.95 a	15.56 a	1.56 a	5.67 a
50	5.58 b	11.73 b	1.22 b	4.42 b	8.81 a	17.82 a	1.81 a	6.53 a
100	4.78ab	10.02 ab	1.03 ab	3.77 ab	8.29 a	16.11 a	1.58 a	5.66 a

Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Appendix

Table B.14: Influence of graded REE applications on mean of REE uptake (µg pot^{-1}) by maize 66 days after sowing (2006)

Application rate	**Uptake by maize roots (µg pot^{-1})**				**Uptake by maize shoots (µg pot^{-1})**			
(µg g^{-1})	**La**	**Ce**	**Pr**	**Nd**	**La**	**Ce**	**Pr**	**Nd**
Lanthanum								
0	43.2 a	89.9 ab	9.1 a	33.4 a	1.6	3.8	----*	1.0
1.0	37.9 a	75.1 ab	7.6 a	27.6 a	1.2	1.7	---*	-----*
10	79.9 ab	73.6 ab	7.6 a	27.6 a	2.9	2.9	----*	1.3
50	192.0 b	66.9 a	6.8 a	24.8 a	nd*	nd	-----*	----*
100	646.5 c	106.8 b	10.8 a	39.2 a	22.7	2.9	----*	-----*
Cerium								
0	43.2 a	89.9 a	9.1 a	33.4 a	1.6	3.8	----**	1.0 a
0.8	45.3 a	100.7 a	9.9 a	36.1 a	2.2	4.0	-----**	1.6 a
8.0	42.3 a	142.6 a	9.5 a	34.5 a	1.5	5.0	-----**	1.5 a
40	53.8 a	337.5 a	12.2 a	43.7 a	1.5	7.2	----**	1.7 a
80	51.5 a	627.7 b	11.5 a	41.2 a	1.6	13.3	-----**	1.4 a
REE-fertilizer								
0	43.2 a	89.9 a	9.1 a	33.4 a	1.6 ab	3.8 ab	----**	1.0
2.7	48.2 ab	100.4 ab	10.4 ab	37.2 ab	1.3 a	1.8 a	-----**	1.4
27	89.4 b	174.3 b	17.7 b	60.3 b	3.4 a	5.3 ab	-----**	1.7
135	252.5 c	432.3 c	43.5 c	141.0 c	8.1 b	9.6 b	0.5	3.1
270	406.8 d	617.4 d	61.2 d	194.4 d	14.7 c	16.2 c	1.6	5.2
Calcium								
0	43.2 a	89.9 a	9.1 a	33.4 a	1.6	3.8	----**	1.0
1.0	43.3 a	93.2 a	9.5 a	34.5 a	1.0	2.3	-----**	----**
10	48.6 a	102.4 a	10.6 a	38.8 a	1.9	2.7	-----**	1.8
50	57.9 a	90.8 a	12.6 a	45.9 a	1.2	1.5	-----**	----**
100	43.4 a	99.6 a	9.4 a	34.2 a	1.5	1.8	-----**	1.2

* nd, no data ** < lower limit of quantitation
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Table B.15: Influence of graded REE applications on mean of REE uptake (µg pot^{-1}) by oilseed rape 66 days after sowing (2006)

Application rate	**Uptake by oilseed rape roots (µg pot^{-1})**				**Uptake by oilseed rape shoots (µg pot^{-1})**			
(µg g^{-1})	**La**	**Ce**	**Pr**	**Nd**	**La**	**Ce**	**Pr**	**Nd**
Lanthanum								
0	43.3 a	86.3 a	8.6 a	30.7 a	2.1 a	3.6 a	1.1	1.2 a
1.0	49.0 a	86.4 a	8.7 a	31.2 a	2.4 a	2.9 a	0.4	1.0 a
10	93.2 a	71.4 a	7.1 a	25.5 a	8.6 a	4.0 a	0.7	1.4 a
50	288.9 b	69.1 a	6.6 a	23.5 a	32.0 b	4.5 a	0.9	1.6 a
100	560.9 c	81.9 a	8.0 a	28.6 a	59.5 c	6.3 a	0.9	2.3 a
Cerium								
0	43.3 a	86.3 a	8.6 a	30.7 a	2.1 a	3.6 a	----*	1.2 a
0.8	32.7 a	69.8 a	6.5 a	23.5 a	2.3 a	3.2 a	----*	1.2 a
8.0	36.8 a	108.7 a	7.2 a	25.9 a	1.7 a	6.4 a	-----*	0.9 a
40	35.7 a	239.7 b	7.1 a	25.2 a	1.7 a	18.4 b	-----*	1.0 a
80	33.8 a	432.7 c	6.9 a	23.1 a	1.7 a	30.4 c	-----*	0.9 a
REE-fertilizer								
0	43.3 a	86.3 a	8.6 a	30.7 a	2.1 a	3.6 a	1.1	1.2 a
2.7	46.6 a	86.9 a	8.7 a	30.4 a	2.3 a	3.5 a	0.7	1.2 a
27	112.9 a	189.7 a	19.1 a	61.9 a	7.7 a	11.1 a	1.1	3.4 a
135	401.7 b	628.0 b	61.0 b	189.5 b	21.9 b	33.0 b	3.6	12.1 b
270	497.3 b	723.1 b	67.5 b	207.5 b	34.8 c	53.0 c	5.7	18.8 c
Calcium								
0	43.3 a	86.3 a	8.6 a	30.7 a	2.1 a	3.6 a	-----*	1.2 a
1.0	40.1 a	80.0 a	8.0 a	29.3 a	1.3 a	1.9 a	------*	0.7 a
10	35.6 a	70.0 a	7.0 a	25.6 a	1.5 a	2.3 a	------*	0.8 a
50	40.7 a	82.5 a	8.4 a	30.3 a	1.3 a	2.1 a	-----*	0.7 a
100	30.4 a	58.4 a	5.7 a	20.5 a	1.4 a	2.2 a	------*	0.8 a

* < lower limit of quantitation
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Appendix

Table B.16a: Correlation coefficients (r) for the relation between **concentration** of REE for **oilseed rape** roots and soil pH and EC 66 days after sowing (2006) (n= 102)

		Roots				Soil pH	Soil EC
		La	**Ce**	**Pr**	**Nd**		
	La	-	.67**	.77**	.77**	.19*	.28**
Roots	**Ce**		-	.92**	.91**	.23*	.39**
	Pr			-	1.00**	.21*	.36**
	Nd				-	.20*	.35**
Soil pH						-	.15
Soil EC							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed).

Table B.16b: Correlation coefficients (r) for the relation between **concentration** of REE for **oilseed rape** shoots and soil pH and EC 66 days after sowing (2006) (n= 102)

		Shoots				Soil pH	Soil EC
		La	**Ce**	**Pr**	**Nd**		
	La	-	.46**	.36	.59**	.14	.19
	Ce		-	.99**	.86**	.30**	.43**
Shoots	**Pr**			-	.99**	.47*	.52**
	Nd				-	.24*	.41**
Soil pH						-	.15
Soil EC							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Table B.16c: Correlation coefficients (r) for the relation between **uptake** of REE for **oilseed rape** roots and soil pH and EC 66 days after sowing (2006) (n= 102)

		Roots				Soil pH	Soil EC
		La	**Ce**	**Pr**	**Nd**		
	La	-	.56**	.67**	.67**	.17	.21*
Roots	**Ce**		-	.90**	.89**	.20*	.29**
	Pr			-	.99**	.18	.28**
	Nd				-	.17	.27**
Soil pH						-	.15
Soil EC							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Table B.16d: Correlation coefficients (r) for the relation between **uptake** of REE for **oilseed rape** shoots and soil pH and EC 66 days after sowing (2006) (n= 102)

		Shoots				Soil pH	Soil EC
		La	**Ce**	**Pr**	**Nd**		
	La	-	.49**	.39*	.62**	.11	.21*
	Ce		-	.99**	.86**	.25*	.43**
Shoots	**Pr**			-	.99**	.34	.55**
	Nd				-	.18	.42**
Soil pH						-	.15
Soil EC							-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed)

Appendix

Table B.17: Influence of graded REE applications on mean of essential nutrients concentration in **shoots of maize** 66 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	---------------(%)------------				--------------(µg g^{-1})-----------------				
Lanthanum									
0	0.14	2.86	0.49	0.16	54.7	269.0	76.0	11.0	<11.1*
1.0	0.13	2.89	0.42	0.16	70.0	290.0	59.0	9.0	<11.0
10	0.12	2.25	0.39	0.17	74.3	159.6	53.2	9.8	<10.8
50	---**	---**	---**	---**	----**	----**	---**	---**	----**
100	0.09	1.36	0.43	0.13	55.0	75.5	65.4	8.9	<11.0
Cerium									
0	0.14 a	2.86 b	0.49 b	0.16 a	54.7 a	269.0 a	76.0 a	11.0 b	<11.1
0.8	0.11 a	1.88 a	0.30 a	0.16 a	87.9 a	137.0 a	59.4 a	8.8 ab	<10.5
8.0	0.12 a	1.87 a	0.32 a	0.80 a	79.2 a	159.4 a	55.8 a	8.8 ab	<10.7
40	0.11 a	1.82 a	0.33 a	0.15 a	85.7 a	132.4 a	64.0 a	8.4 a	<10.1
80	0.11 a	1.77 a	0.35 a	0.14 a	103.3 a	162.0 a	59.8 a	8.0 a	<10.1
REE-fertilizer									
0	0.14 ab	2.86 ab	0.49 a	0.16 a	54.7 a	269.0 a	76.0a b	11.0 b	<11.1
2.7	0.11 a	1.70 a	0.34 a	0.15 a	165.4 b	204.0 a	74.5 ab	6.0 a	<10.3
27	0.10 a	1.72 a	0.39 a	0.15 a	160.0 b	211.2 a	63.0 ab	7.3 a	<10.3
135	0.13 ab	2.42 a	0.34 a	0.13 a	192.7 b	269.3 a	58.7 a	7.5 a	<10.6
270	0.17 b	4.06 b	0.48 a	0.15 a	201.4 b	329.0 a	91.5 b	8.3 ab	< 9.6
Calcium									
0	0.14 a	2.86 a	0.49 c	0.16 a	54.7 a	269.0 a	76.0 b	11.0 b	<11.1
1.0	0.11 a	1.99 a	0.29 a	0.14 a	120.7 b	120.2 a	76.0 ab	7.7 a	<10.8
10	0.11 a	2.02 a	0.33 ab	0.16 a	131.8 b	145.6 a	46.0 b	7.4 a	< 9.7
50	0.10 a	1.63 a	0.41 abc	0.14 a	133.5 b	192.8 a	65.0 ab	6.2 a	<10.3
100	0.12 a	2.16 a	0.47 bc	0.15 a	148.3 b	223.4 a	59.6 ab	6.4 a	< 9.9

* < lower limit of quantitation ** no data

Table B.18: Influence of graded REE applications on mean of essential nutrients concentration in **shoots of oilseed rape** 66 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	---------------(%)------------				--------------(µg g^{-1})-----------------				
Lanthanum									
0	0.32 b	3.22 a	1.23 a	0.22 a	181.1 a	518.0 ab	94.0 a	8.6 a	11.3 a
1.0	0.29 b	3.04 a	1.15 a	0.20 a	89.2 a	485.5 ab	98.7 a	7.7 a	10.2 a
10	0.29 b	3.11 a	1.22 a	0.20 a	105.3 a	459.0 a	96.3 a	7.7 a	10.1 a
50	0.33 b	3.17 a	1.22 a	0.21 a	134.2 a	533.7 ab	94.7 a	7.7 a	11.1 a
100	0.32 a	3.16 a	1.11 a	0.19 a	157.8 a	597.3 b	93.3 a	7.0 a	10.4 a
Cerium									
0	0.32 ab	3.22 ab	1.23 a	0.22 a	181.1 b	518.0 a	94.0 ab	8.6 a	11.3 a
0.8	0.39 b	3.69 b	1.06 a	0.19 a	126.3 ab	457.0 a	79.0 a	7.5 a	11.9 a
8.0	0.28 a	2.87 a	1.12 a	0.18 a	103.8 a	450.2 a	101.3 b	7.0 a	10.3 a
40	0.31 ab	2.79 a	1.06 a	0.18 a	114.8 ab	442.8 a	87.8 ab	6.8 a	10.5 a
80	0.27 a	2.86 a	1.16 a	0.18 a	106.8 a	499.7 a	93.8 ab	8.0 a	10.9 a
REE-fertilizer									
0	0.32 a	3.22 a	1.23 a	0.22 a	181.1 b	518.0 a	94.0 b	8.6 a	11.3 a
2.7	0.32 a	2.94 a	1.14 a	0.19 a	62.9 a	498.0 a	60.2 a	7.2 a	12.7 a
27	0.39 a	3.21 a	1.13 a	0.18 a	75.6 a	647.2 ab	76.5 ab	8.2 a	13.4 a
135	0.35 a	2.95 a	1.23 a	0.21 a	92.6 a	608.2 ab	67.3 a	8.0 a	13.3 a
270	0.37 a	3.08 a	1.13 a	0.18 a	98.0 a	772.3 b	73.3 ab	8.0 a	13.1 a
Calcium									
0	0.32 a	3.22 b	1.23 a	0.22 b	181.1 b	518.0 a	94.0 a	8.6 a	11.3 ab
1.0	0.32 a	3.06 ab	1.17 a	0.20 ab	98.8 a	487.0 a	92.2 a	8.3 a	10.5 a
10	0.30 a	2.86 ab	1.09 a	0.18 ab	108.1 a	474.5 a	85.0 a	7.8 a	10.9 ab
50	0.30 a	2.85 a	1.17 a	0.17 a	74.8 a	473.5 a	99.5 a	7.3 a	11.3 ab
100	0.33 a	2.94 ab	1.24 a	0.19 ab	61.5 a	516.7 a	87.7 a	7.8 a	11.9 b

Appendix

Table B.19: Influence of graded REE applications on mean of essential nutrients concentration in **roots of maize** 66 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	(%)				(µg g^{-1})				
Lanthanum									
0	0.18 a	1.67 b	0.69 a	0.33 bc	2618.3 a	465.2 a	46.0 a	16.2 ab	10.7 a
1.0	0.18 a	1.77 b	0.85 a	0.34 bc	2060.9 a	484.2 a	59.7 a	22.7 c	15.7 b
10	0.19 a	1.56 ab	0.84 a	0.30 c	2285.5 a	530.8 a	40.5 a	22.8 c	15.3 b
50	0.18 a	1.44 ab	0.79 a	0.27 ab	2107.9 a	521.7 a	56.0 a	20.3 bc	13.9 ab
100	0.16 a	1.20 a	0.73 a	0.21 a	2478.9 a	407.8 a	40.6 a	14.4 a	15.1 b
Cerium									
0	0.18 a	1.67 a	0.69 a	0.33 a	2618.3 a	465.2 a	46.0 ab	16.2 b	10.7 a
0.8	0.18 a	1.57 a	0.79 a	0.29 a	2239.5 a	533.5 a	37.0 a	13.0 a	12.9 b
8.0	0.18 a	1.69 a	0.81 a	0.33 a	2381.8 a	574.7 a	66.2 b	13.0 a	14.3 b
40	0.17 a	1.54 a	0.69 a	0.31 a	2656.5 a	523.5 a	39.5 a	12.2 a	14.2 b
80	0.18 a	1.68 a	0.78 a	0.32 a	2437.9 a	562.5 a	43.3 ab	12.5 a	14.2 b
REE-fertilizer									
0	0.18 a	1.67 b	0.69 a	0.33 a	2618.3 ab	465.2 a	46.0 a	16.2 ab	10.7 a
2.7	0.19 a	1.64 b	0.86 b	0.36 a	2318.9 a	512.2 ab	49.2 a	14.7 a	13.6 b
27	0.18 a	1.07 a	0.80 ab	0.36 a	3215.7 bc	607.2 ab	75.3 ab	14.3 a	15.4 bc
135	0.19 a	1.08 a	0.81 ab	0.41 a	3255.1 bc	682.0 b	60.5 b	15.2 ab	14.7 bc
270	0.21 a	1.28 a	0.73 ab	0.39 a	3489.4 c	560.3 ab	83.7 b	19.3 a	16.2 c
Calcium									
0	0.18 a	1.67 a	0.69 a	0.33 a	2618.3 ab	465.2 a	46.0 a	16.2 b	10.7 a
1.0	0.17 a	1.34 a	0.69 a	0.32 a	2281.3 a	485.2 a	57.8 a	12.2 a	15.1 b
10	0.17 a	1.69 a	0.79 ab	0.34 a	2544.9 ab	562.5 a	52.5 a	11.7 a	15.2 b
50	0.18 a	1.36 a	0.79 ab	0.35 a	3113.2 b	603.2 a	69.3 a	12.2 a	15.1 b
100	0.19 a	1.36 a	0.92 b	0.38 a	2730.5 ab	622.0 a	64.3 a	12.0 a	14.2 b

Table B.20: Influence of graded REE applications on mean of essential nutrients concentration in **roots of oilseed rape** 66 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	(%)				(µg g^{-1})				
Lanthanum									
0	0.28 a	1.04 b	0.53 a	0.19 a	5312.3 a	672.7 a	95.2 a	33.8 a	24.0 a
1.0	0.24 a	0.82 a	0.53 a	0.19 a	5620.7 a	731.5 a	98.3 a	32.5 a	23.5 a
10	0.26 a	0.88 ab	0.53 a	0.19 a	5540.9 a	676.8 a	118.3 a	37.5 a	24.6 a
50	0.24 a	0.88 ab	0.48 a	0.19 a	5488.0 a	726.5 a	95.3 a	33.5 a	23.8 a
100	0.24 a	0.81 a	0.45 a	0.17 a	5509.2 a	703.0 a	90.0 a	33.5 a	23.4 a
Cerium									
0	0.28 a	1.04 b	0.53 a	0.19 a	5312.3 a	672.7 a	95.2 a	33.8 a	24.0 a
0.8	0.27 a	0.87 ab	0.59 a	0.19 a	5465.5 a	670.5 a	115.0 a	37.0 a	23.5 a
8.0	0.26 a	0.83 a	0.52 a	0.17 a	5381.3 a	686.3 a	92.7 a	37.3 a	23.5 a
40	0.26 a	0.79 a	0.42 a	0.18 a	5997.4 a	627.8 a	99.0 a	38.8 a	24.3 a
80	0.28 a	0.95 ab	0.49 a	0.18 a	5201.6 a	670.8 a	113.8 a	35.7 a	23.9 a
REE-fertilizer									
0	0.28 a	1.04 a	0.53 a	0.19 ab	5312.3 a	672.7 a	95.2a	33.8 a	24.0 bc
2.7	0.27 a	0.89 a	0.62 a	0.19 b	5400.3 a	825.5 ab	123.5 ab	40.3 a	26.2 c
27	0.29 a	0.87 a	0.57 a	0.18 ab	4936.2 a	878.8 ab	112.7 ab	41.8 a	26.0 c
135	0.31 a	0.89 a	0.62 a	0.19 b	4748.5 a	838.2 ab	110.7 ab	38.3 a	22.9 b
270	0.31 a	0.89 a	0.58 a	0.16 a	3955.1 a	1114.2 b	139.8 b	40.5 a	17.3 a
Calcium									
0	0.28 a	1.04 a	0.53 a	0.19 a	5312.3 a	672.7 a	95.2 a	33.8 a	24.0 ab
1.0	0.26 a	0.95 a	0.55 a	0.19 a	5136.2 a	734.3 ab	94.8 a	34.2 a	24.6 ab
10	0.26 a	0.97 a	0.58 a	0.19 a	4576.8 a	723.3 ab	120.2 a	33.0 a	22.9 a
50	0.22 a	0.79 a	0.49 a	0.17 a	5559.0 a	702.0 ab	97.8 a	32.0 a	23.4 ab
100	0.28 a	0.93 a	0.63 a	0.18 a	5247.5 a	965.5 b	108.0 a	38.8 a	24.9 b

Appendix

Table B.21: Influence of graded REE applications on mean of essential nutrients concentration in **shoots of maize** 35 days after sowing (2006)

Application rate ($\mu g\ g^{-1}$)	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	---------------(%)------------				--------------($\mu g\ g^{-1}$)-----------------				
Lanthanum									
0	0.27 a	7.68 a	0.68 ab	0.31 a	200.4 b	159.2 a	75.7 a	16.3 a	11.1 a
1.0	0.28 a	7.78 a	0.67 ab	0.33 a	140.4 a	171.2 a	83.5 a	16.8 a	10.4 a
10	0.28 a	7.69 a	0.68 ab	0.33 a	138.0 a	158.8 a	61.7 a	18.5 a	9.6 a
50	0.28 a	7.89 a	0.65 a	0.32 a	146.9 ab	176.3 a	62.2 a	17.3 a	10.3 a
100	0.29 a	7.75 a	0.82 b	0.35 a	143.6 a	184.5 a	61.8 a	17.7 a	10.1 a
Cerium									
0	0.27 a	7.68 a	0.68 a	0.31 a	200.4 b	159.2 a	75.7 a	16.3 a	11.1 ab
0.8	0.29 a	7.74 a	0.71 a	0.33 a	137.5 ab	181.0 ab	55.5 a	18.2 a	11.2 ab
8.0	0.29 a	7.77 a	0.69 a	0.33 a	173.2 ab	187.5 b	61.3 a	18.3 a	12.2 ab
40	0.29 a	7.91 a	0.65 a	0.32 a	175.5 ab	170.3 ab	56.8 a	19.0 a	10.1 a
80	0.28 a	7.97 a	0.79 a	0.34 a	117.0 a	224.2 c	65.7 a	17.7 a	13.1 b
REE-fertilizer									
0	0.27 a	7.68 b	0.68 a	0.31 a	200.4 a	159.2 a	75.7 a	16.3 a	11.1 a
2.7	0.29 b	8.34 c	0.69 a	0.32 a	168.9 a	169.0 a	58.0 a	24.0 ab	12.6 ab
27	0.30 b	8.32 c	0.67 a	0.32 a	133.9 a	153.2 a	67.2 a	21.8 ab	12.0 ab
135	0.30 b	7.85 bc	0.68 a	0.29 a	133.7 a	160.5 a	57.7 a	19.8 b	13.9 bc
270	0.30 b	7.03 a	0.93 b	0.32 a	116.5 a	244.7 b	79.8 a	31.8 b	15.5 c
Calcium									
0	0.27 a	7.68 a	0.68 a	0.31 a	200.4 b	159.2 a	75.7 a	16.3 ab	11.1 ab
1.0	0.28 a	8.24 a	0.59 a	0.32 a	116.4 a	152.5 a	56.7 a	15.5 a	9.9 a
10	0.29 a	7.97 a	0.65 a	0.32 a	116.2 a	153.5 a	66.0 a	18.8 bc	12.1 ab
50	0.29 a	8.07 a	0.69 a	0.31 a	156.2 ab	142.5 a	58.7 a	20.2 c	11.3 ab
100	0.29 a	7.92 a	0.88 b	0.31 a	124.6 a	161.5 a	60.2 a	20.7 c	12.9 b

Table B.22: Influence of graded REE applications on mean of essential nutrients concentration in **shoots of oilseed rape** 35 days after sowing (2006)

Application rate ($\mu g\ g^{-1}$)	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	---------------(%)------------				--------------($\mu g\ g^{-1}$)-----------------				
Lanthanum									
0	0.98 ab	9.02 ab	1.54 ab	0.46 a	125.8 a	198.8 a	100.6 a	18.6 b	28.5 a
1.0	0.93 a	9.11 ab	1.49 ab	0.47 a	128.6 a	216.5 a	100.5 a	15.3 ab	29.9 a
10	0.89 a	8.45 a	1.40 a	0.45 a	111.0 a	208.6 a	103.6 a	11.4 a	28.5 a
50	0.96 ab	9.00 ab	1.47 ab	0.46 a	126.0 a	235.8 a	99.3 a	17.8 b	29.8 a
100	1.09 b	9.79 b	1.66 b	0.54 b	144.9 a	323.2 b	11.3 a	14.7 ab	34.2 b
Cerium									
0	0.98 a	9.02 a	1.54 a	0.46 a	125.8 a	198.8 a	100.6 a	18.6 b	28.5 a
0.8	1.09 a	9.90 ab	1.93 a	0.61 a	128.4 a	298.5 a	127.5 a	14.2 a	35.3 a
8.0	1.03 a	9.53 a	1.69 a	0.50 a	116.4 a	246.8 a	95.3 a	12.0 a	33.3 a
40	1.01 a	9.92 ab	1.50 a	0.51 a	123.2 a	230.2 a	93.8 a	11.8 a	31.5 a
80	1.28 a	10.94b	1.68 a	0.58 a	118.2 a	211.0 a	107.8 a	11.8 a	34.2 a
REE-fertilizer									
0	0.98 a	9.02 a	1.54 a	0.46 a	125.8 a	198.8 a	100.6 a	18.6 b	28.5 a
2.7	1.07 ab	9.67 a	1.42 a	0.48 a	227.5 b	224.8 ab	94.2 a	11.3 a	29.7 ab
27	1.11 b	9.41 a	1.48 a	0.46 a	243.6 b	230.3 ab	89.0 a	11.5 a	31.6 b
135	1.15 b	9.40 a	1.63 a	0.51 a	233.7 b	261.8 b	100.2 a	11.2 a	31.0 ab
270	1.03 ab	8.88 a	1.68 a	0.49 a	270.9 b	278.5 b	106.3 a	10.8 a	29.6 ab
Calcium									
0	0.98	9.02	1.54	0.46	125.8	198.8	100.6	18.6	28.5
1.0	1.05	9.98	1.48	0.49	96.1	225.0	89.6	9.9	30.5
10	----*	-----*	-----*	-----*	-----*	-----*	-----*	-----*	----*
50	1.06	9.89	1.61	0.48	241.2	239.4	87.8	10.1	31.3
100	1.15	9.94	1.87	0.58	244.4	278.1	107.7	11.4	30.1

* no data

Appendix

Table B.23: Influence of graded REE applications on mean of essential nutrients concentration in **roots of maize** and 35 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	---------------(%)------------				--------------(µg g^{-1})-----------------				
Lanthanum									
0	0.32a	4.28a	0.87a	0.40a	787.1a	98.0a	183.2a	20.0a	9.0
1.0	0.31a	4.07a	0.81a	0.39a	815.2a	136.3ab	150.2a	20.5a	7.1
10	0.31a	4.11a	0.85a	0.41a	705.4a	124.3a	145.0a	21.5a	7.6
50	0.29a	4.29a	0.83a	0.37a	749.1a	147.7ab	141.5a	18.5a	9.6
100	0.33a	4.87a	0.92a	0.42a	609.7a	194.0b	150.5a	23.3a	8.3
Cerium									
0	0.32a	4.28a	0.87a	0.40a	787.1a	98.0a	183.2a	20.0a	9.0
0.8	0.31a	4.66a	0.86a	0.43a	672.7a	133.8a	136.2a	22.3a	7.8
8.0	0.34a	4.65a	0.84a	0.41a	960.6a	159.8ab	119.8a	24.0a	10.2
40	0.32a	4.51a	0.83a	0.37a	694.8a	150.5a	130.5a	22.0a	7.8
80	0.36a	4.73a	1.07a	0.48a	681.9a	229.2b	167.2a	22.0a	7.9
REE-fertilizer									
0	0.32a	4.28ab	0.87ab	0.40a	787.1a	98.0a	183.2c	20.0ab	9.0
2.7	0.32a	5.01b	0.89ab	0.39a	773.1a	134.0ab	175.0bc	16.2ab	6.9
27	0.31a	4.41ab	0.79ab	0.37a	679.8a	112.3ab	142.8ab	14.0a	7.3
135	0.31a	3.93a	0.74a	0.41a	669.9a	153.3b	141.3ab	15.5ab	9.8
270	0.31a	4.19b	0.99b	0.41a	819.9a	287.7c	132.5a	22.7b	11.1
Calcium									
0	0.32a	4.28a	0.87a	0.40a	787.1a	98.0a	183.2a	20.0a	9.0
1.0	0.33a	4.79a	0.75a	0.37a	699.0a	125.0a	110.5a	18.0a	8.8
10	0.34a	4.59a	0.93a	0.40a	773.2a	121.7a	160.7a	18.2a	10.7
50	0.34a	4.28a	0.92a	0.37a	751.8a	119.0a	125.0a	15.5a	7.1
100	0.37a	5.20a	1.20b	0.39a	663.8a	135.2a	171.5a	16.7a	8.0

Table B.24: Influence of graded REE applications on mean of essential nutrients concentration in roots of oilseed rape 35 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	---------------(%)------------				--------------(µg g^{-1})-----------------				
Lanthanum									
0	0.32	4.48	0.33	0.11	841.7	86.2	80.8	30.0	43.1
1.0	0.31	4.71	0.41	0.12	495.0	88.2	113.5	13.0	17.9
10	0.31	4.67	0.39	0.12	353.8	89.6	69.0	9.6	18.5
50	0.29	4.56	0.31	0.12	485.9	99.7	67.8	12.8	17.7
100	0.33	4.55	0.47	0.17	1061.9	142.2	114.0	29.7	18.4
Cerium									
0	0.32	4.48	0.33	0.11	841.7	86.2	80.8	30.0	43.1
0.8	0.31	4.95	0.36	0.13	639.2	112.2	90.8	11.8	<8.5*
8.0	0.34	4.66	0.35	0.13	358.8	107.3	72.0	12.0	20.7
40	0.32	4.74	0.45	0.11	400.8	101.5	87.2	11.5	17.9
80	0.36	5.06	0.39	0.11	229.9	99.5	61.2	10.2	18.4
REE-fertilizer									
0	0.32	4.48	0.33	0.11	841.7	86.2	80.8	30.0	43.1
2.7	0.32	4.44	0.48	0.11	391.6	112.3	75.3	15.5	16.9
27	0.31	5.36	0.64	0.13	464.9	128.0	98.5	28.0	17.9
135	0.31	4.82	0.56	0.12	362.6	112.7	90.0	12.2	16.4
270	0.31	4.60	0.49	0.24	585.7	150.0	109.2	19.0	18.1
Calcium									
0	0.32	4.48	0.33	0.11	841.7	86.2	80.8	30.0	43.1
1.0	0.33	4.96	0.33	0.10	310.6	101.2	80.0	10.0	16.4
10	0.34	4.92	0.35	0.10	384.8	97.8	77.5	11.3	16.3
50	0.34	5.02	0.45	0.11	399.9	101.8	67.7	12.7	18.4
100	0.37	4.57	0.39	0.12	550.7	136.3	92.8	19.7	15.8

* < lower limit of quatitation

Appendix

Table B.25: Influence of graded REE applications on mean of essential nutrients **uptake** by roots of maize 66 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	Uptake (mg pot^{-1})							Uptake (µg pot^{-1})	
Lanthanum									
0	18.27 a	171.40 a	68.53 a	32.06 c	26.4 ab	4.6 a	0.45 a	161.4 a	107.4 a
1.0	17.55 a	171.06 a	79.58 a	31.43 bc	19.6 a	4.3 a	0.55 a	221.0 a	144.9 a
10	16.46 a	139.19 a	74.33 a	32.65 c	20.3 ab	4.5 a	0.36 a	204.6 a	138.1 a
50	16.02 a	132.89 a	71.86 a	24.19 ab	18.7 a	4.5 a	0.49 a	187.9 a	126.3 a
100	18.66 a	137.09 a	83.20 a	23.49 a	28.9 a	4.7 a	0.46 a	162.4 a	173.4 a
Cerium									
0	18.27 a	171.40 a	68.53 a	32.06 a	26.4 a	4.6 a	0.45 a	161.4 a	107.4 a
0.8	19.80 a	174.90 a	89.00 b	33.00 a	25.7 a	5.9 a	0.42 a	161.4 a	147.5 ab
8.0	19.60 a	183.90 a	88.10 b	35.40 a	26.3 a	6.2 a	0.70 b	148.2 a	156.3 ab
40	20.50 a	179.80 a	81.00 ab	37.10 a	32.1 a	6.1 a	0.46 ab	143.3 a	168.9 b
80	21.40 a	197.40 a	92.40 b	37.20 a	29.6 a	6.5 a	0.52 ab	146.5 a	170.5 b
REE-fertilizer									
0	18.27 b	171.40 b	68.53 bc	32.06 b	26.4 b	4.6 b	0.45 ab	161.4 c	107.4 b
2.7	19.43 b	165.46 b	86.16 b	35.76 b	23.8 b	5.2 b	0.49 bc	149.0 bc	138.3 b
27	15.83 b	89.96 a	70.65 bc	31.95 b	28.5 b	5.4 b	0.66 c	126.6 bc	135.7 b
135	14.52 b	84.90 a	62.64 c	31.07 b	25.2 b	5.1 b	0.46 ab	115.6 b	113.6 b
270	7.73 a	49.94 a	28.80 a	15.21 a	13.3 a	2.4 a	0.31 a	70.2 a	62.2 a
Calcium									
0	18.27 a	171.40 a	68.53 a	32.06 a	26.4 a	4.6 a	0.45 a	161.4 b	107.4 a
1.0	17.75 a	138.37 a	74.13 a	32.32 a	24.8 a	5.1 a	0.61 a	128.8 ab	161.4 a
10	17.63 a	170.62 a	80.55 a	34.11 a	26.6 a	5.7 a	0.53 a	121.1 ab	157.8 a
50	18.35 a	137.90 a	79.44 a	34.74 a	32.2 a	5.9 a	0.71 a	124.3 ab	153.5 a
100	17.86 a	126.83 a	84.24 a	34.48 a	24.7 a	5.6 a	0.59 a	107.9 a	130.1 a

Table B.26: Influence of graded REE applications on mean of essential nutrients **uptake** by shoots of maize 66 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu
	Uptake (mg pot^{-1})							Uptake (µg pot^{-1})
Lanthanum								
0	23.58	470.92	80.80	27.05	0.9	4.4	1.3	181.2
1.0	23.08	509.83	74.98	27.88	1.2	5.1	1.1	155.7
10	21.58	396.30	69.12	30.28	1.3	2.8	0.9	173.3
50	----*	----*	----*	---*	---*	----*	----*	-----*
100	20.59	316.03	98.72	30.58	1.3	1.8	1.6	215.2
Cerium								
0	23.58 a	470.92 a	80.80 a	27.05 a	0.9 a	4.4 a	1.3 a	181.2 a
0.8	26.00 a	444.00 a	72.20 a	37.30 a	2.1 ab	3.2 a	1.4 a	205.7 a
8.0	28.80 a	465.40 a	78.80 a	43.70 a	2.0 ab	4.0 a	1.4 a	220.7 a
40	27.50 a	449.80 a	80.70 a	38.00 a	2.1 ab	3.3 a	1.6 a	208.7 a
80	25.10 a	412.10 a	83.20 a	33.50 a	2.5 b	3.8 a	1.4 a	185.2 a
REE-fertilizer								
0	23.58 bc	470.92 a	80.80 b	27.05 b	0.9 a	4.4 a	1.3 a	181.2 b
2.7	22.84 ab	355.70 a	72.88 ab	31.99 b	3.4 bc	4.3 a	1.6 a	128.2 ab
27	23.02 ab	383.22 a	87.36 b	31.97 b	3.6 c	4.8 a	1.4 a	160.1 b
135	25.27 b	466.46 a	67.30 ab	26.45 b	3.9 c	5.3 a	1.2 a	146.7 b
270	15.72 a	358.34 a	44.29 a	13.97 a	1.9 ab	3.2 a	0.9 a	77.8 a
Calcium								
0	23.58 a	470.92 a	80.80 a	27.05 a	0.9 a	4.4 a	1.3 ab	181.2 a
1.0	25.97 a	439.61 a	66.32 a	32.73 a	2.7 b	2.5 a	1.1 a	176.7 a
10	25.49 a	456.76 a	75.95 a	38.27 a	3.0 b	3.2 a	1.6 b	172.0 a
50	23.67 a	371.22 a	94.02 a	31.69 a	3.0 b	4.4 a	1.5 ab	138.9 a
100	23.82 a	409.24 a	91.14 a	29.52 a	2.9 b	4.3 a	1.2 ab	126.3 a

* no data

Appendix

Table B.27: Influence of graded REE applications on mean of essential nutrients **uptake** by oilseed rape roots 66 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	Uptake (mg pot^{-1})							Uptake (µg pot^{-1})	
Lanthanum									
0	12.43 b	1.04 a	25.60 a	8.40 a	23.6 a	3.0 a	0.42 a	149.2 a	106.6 a
1.0	10.20 ab	0.82 a	21.70 a	8.20 a	24.2 a	3.1 a	0.41 a	136.9 a	99.4 a
10	10.10 ab	0.87 a	20.30 a	7.60 a	22.5 a	2.7 a	0.45 a	145.0 a	97.2 a
50	9.30 a	0.88 a	18.10 a	7.30 a	20.8 a	2.8 a	0.36 a	126.9 a	90.5 a
100	10.70 ab	0.82 a	19.60 a	7.70 a	24.8 a	3.1 a	0.39 a	149.2 a	104.7 a
Cerium									
0	12.43 a	1.04 a	25.60 a	8.40 a	23.6 a	3.0 a	0.42 a	149.2 a	106.6 a
0.8	9.87 a	0.87 a	22.50 a	7.28 a	20.7 a	2.6 a	0.44 a	134.7 a	87.7 a
8.0	10.83 a	0.83 a	21.68 a	7.26 a	22.9 a	2.9 a	0.39 a	156.0 a	98.6 a
40	9.97 a	0.79 a	16.35 a	6.89 a	22.8 a	2.4 a	0.38 a	145.8 a	92.9 a
80	9.99 a	0.95 a	18.33 a	6.60 a	19.8 a	2.5 a	0.41 a	129.4 a	87.9 a
REE-fertilizer									
0	12.43 b	1.04 b	25.60 a	8.40 a	23.6 a	3.0 a	0.42 a	149.2 a	106.6 b
2.7	10.67 ab	0.89 ab	24.63 a	7.85 a	22.0 a	3.3 a	0.49 a	156.9 a	104.6 b
27	10.09 ab	0.87 a	21.76 a	6.81 a	18.5 a	3.2 a	0.39 a	144.6 a	95.2 b
135	11.91 ab	0.89 ab	23.23 a	7.54 a	18.9 a	3.2 a	0.43 a	146.8 a	90.7 ab
270	9.15 a	0.89 a	16.73 a	5.20 a	12.8 a	2.7 a	0.41 a	121.5 a	53.5 a
Calcium									
0	12.43 a	1.04 b	25.60 a	8.40 a	23.6 a	3.0 a	0.42 ab	149.2 a	106.6 a
1.0	12.40 a	0.95 b	26.40 a	8.8 a	24.4 a	3.6 a	0.45 ab	161.5 a	116.9 a
10	11.20 a	0.97 ab	25.00 a	8.2 a	20.5 a	3.2 a	0.52 b	144.0 a	101.5 a
50	10.10 a	0.79 ab	22.60 a	7.6 a	25.7 a	3.2 a	0.45 ab	146.5 a	107.1 a
100	9.60 a	0.93 a	22.30 a	6.4 a	18.8 a	3.5 a	0.38 a	137.8 a	87.4 a

Table B.28: Influence of graded REE applications on mean of essential nutrients **uptake** by shoots of oilseed rape 66 days after sowing (2006)

Application rate (µg g^{-1})	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	Uptake (mg pot^{-1})							Uptake (µg pot^{-1})	
Lanthanum									
0	30.57 a	288.66 a	112.52 a	20.20 a	1.6 a	4.6 a	0.8 a	76.9 a	97.3 a
1.0	24.20 a	285.20 a	106.00 a	19.00 a	0.8 a	4.5 a	0.9 a	70.7 a	97.9 a
10	26.20 a	276.80 a	106.20 a	17.40 a	0.9 a	4.9 a	3.1 a	60.4 a	84.8 a
50	27.90 a	269.30 a	103.30 a	17.90 a	1.1 a	4.5 a	0.8 a	64.9 a	93.3 a
100	28.60 a	277.00 a	96.60 a	16.80 a	1.4 a	5.2 a	0.8 a	68.9 a	91.3 a
Cerium									
0	30.57 a	288.66 ab	112.52 a	20.20 a	1.6 a	4.6 a	0.8 ab	76.9 a	97.3 a
0.8	33.63 a	320.43 b	93.12 a	16.94 a	1.1 a	4.1 a	0.7 a	67.1 a	105.3 a
8.0	27.66 a	281.21 ab	110.04 a	18.15 a	1.0 a	4.4 a	1.0 b	68.7 a	98.7 a
40	28.27 a	250.88 a	96.01 a	16.56 a	1.0 a	4.1 a	0.8 ab	63.3 a	90.6 a
80	24.77 a	258.59 ab	104.79 a	16.21 a	0.9 a	4.5 a	0.8 ab	72.6 a	97.7 a
REE-fertilizer									
0	30.57 a	288.66 a	112.52 a	20.20 a	1.6 b	4.6 a	0.8 b	76.9 a	97.3 a
2.7	31.50 a	290.71 a	112.57 a	19.54 a	0.6 a	4.9 a	0.6 a	68.8 a	125.5 a
27	37.60 a	309.45 a	110.41 a	18.22 a	0.7 a	6.2 ab	0.7 ab	80.6 a	129.1 a
135	32.10 a	269.57 a	113.66 a	19.18 a	0.8 a	5.5 ab	0.6 a	74.9 a	122.0 a
270	34.80 a	288.95 a	105.21 a	17.19 a	0.9 a	7.2 b	0.7 ab	76.5 a	116.9 a
Calcium									
0	30.57 a	288.66 a	112.52 a	20.20 a	1.6 b	4.6 a	0.8 a	76.9 a	97.3 a
1.0	30.50 a	294.20 a	111.80 a	19.50 a	1.0 a	4.7 a	0.9 a	83.5 a	96.1 a
10	29.60 a	283.30 a	108.20 a	17.70 a	1.1 ab	4.7 a	0.8 a	78.7 a	106.3 a
50	29.40 a	259.20 a	114.60 a	16.70 a	0.7 a	4.6 a	1.0 a	73.7 a	110.9 a
100	33.40 a	293.40 a	125.30 a	19.10 a	0.6 a	5.3 a	0.9 a	80.5 a	106.5 a

Appendix

Table B.29: Correlation coefficients (r) for the relation between concentrations of REE, macro- and micro-nutrients for **maize** and **oilseed rape** 66 days after sowing (2006)

		La	Ce	Pr	Nd	S	K	Ca	Mg	Fe	Cu	Mn	Zn	B
								Roots of maize						
Shoots of maize	**La**	.98**	.92**	.95**	.95**	.47**	- .24	- .08	.28*	.51**	.54**	.05	.46**	.53**
	Ce	-	.96**	.94**	.94**	.36**	- .16	- .09	.30**	.51**	.45**	.12	.37**	.34**
	Pr		-	.93**	.93**	.50	.14	- .31	- .36	.39	.67*	- .52	.58	.68*
	Nd			-	.97**	.57**	- .16	- .11	.37*	.54**	.59**	- .06	.56**	.60**
	S				-	.46**	.07	.02	.51**	.29**	.39**	.09	.39**	.21
	K					-	.16	.08	.61**	.39**	.57**	.23*	.42**	.34**
	Ca						-	.15	.25**	.27*	.34**	.08	.24*	0.17
	Mg							-	- .13	- .21	.12	- .34**	- .13	.004
	Fe								-	.49**	.18	.29**	.56**	.35**
	Cu									-	.32**	.01	- .04	.06
	Mn										-	.54**	.44**	.23**
	Zn											-	.19	.19
	B												-	
								Roots of oilseed rape						
Shoots of oilseed rape	**La**	.81**	.42**	.51**	.51**	.04	- .17	- .008	- .16	- .16	.08	.25*	.09	- .38**
	Ce	-	.92**	.80**	.79**	.34**	.001	- .03	- .18	- .28	.20	.31**	.31**	- 55**
	Pr		-	.89**	.89**	.36	.22	.09	- .19	- 56**	.14	.46*	.39	- .75**
	Nd			-	.95**	.34**	- .01	.06	- .15	- .37**	.21	.45**	.33**	- .62**
	S				-	.39**	.66**	.35**	.24*	- .52**	.73**	.45**	.50**	- .08
	K					-	1.00**	.29**	.34*	- .49**	.29**	.19*	.29**	.07
	Ca						-	1.00**	.38**	- .31**	.37**	.63**	.52**	.07
	Mg							-	1.00**	.02	.22*	.03	.08	.39**
	Fe								-	1.00**	- .29**	- .33**	- .36**	.36**
	Cu									-	1.00**	.44**	..59**	.24*
	Mn										-	1.00**	.51**	- .17
	Zn												1.00**	- .09
	B													- .05

** Correlation significant at the 0.01 level (2-tailed) * Correlation significant at the 0.05 level (2-tailed). n= 102

Appendix

Table B.30: Correlation coefficients (r) for the relation between concentration of REE, macro- and micro-nutrients for **maize** roots and shoots and soil pH and EC 66 days after sowing (2006)

		La	Ce	Pr	Nd	S	K	Ca	Mg	Fe	Cu	Mn	Zn	B	Soil pH	Soil EC
								Roots of maize								
Roots of maize	**La**	-	.88**	.93**	.93**	.32**	- .29**	- .09	.13	.43**	.33**	- .007	.32**	.33**	- .18	.69**
	Ce		-	.97**	.97**	.37**	- .19	- .10	.28**	.51**	.23*	.06	.35**	.32**	- .18	.73**
	Pr			-	1.00**	.41**	- .24*	- .06	.33**	.52**	.29**	.09	.42**	.32*	- .25*	.79**
	Nd				-	.41**	- .24*	- .06	.33**	.53**	.29**	.09	.42**	.32**	- .25*	.79**
	S					-	.23*	.54**	.67**	.28**	.39**	.48**	.38**	.28**	- .44**	.54**
	K						-	.31**	.18	- .53**	.13	.05	- .14	- .19	- .12	- .09
	Ca							-	.57**	- .13	.19*	.048**	.34**	.07	- .33**	.14
	Mg								-	.32**	.20*	.66**	.41**	.21*	- .63**	.61**
	Fe									-	- .02	.33**	.38**	.39**	- .19	.51**
	Cu										-	- .06	.11	.37**	- .17	.31**
	Mn											-	.34**	.16	- .63**	.41**
	Zn												-	.29**	- .29**	.51**
	B													-	- .10	.29**
Soil pH															-	- .64**
Soil EC																-
								Shoots of maize								
Shoots of maize	**La**	-	.83**	.95**	.96**	.45**	.79**	.62**	.006	.49**	.14	.58**	.49**		- .14	.71**
	Ce		-	.99**	.97**	.59**	.78**	.49**	.004	.48**	.24	.59**	.43**		- .22	.76**
	Pr			-	.99**	.48	.77**	.77*	.48	.30	.38	.75*	.52		.45	.76**
	Nd				-	.65**	.88**	.62**	.09	.57**	.21	.72**	.63**		- .29	.87**
	S					-	.86**	.35**	.17	.60**	.37**	.64**	.36**		-.33**	.67**
	K						-	.53**	.20	.52**	.42**	.77**	.39**		- .55**	.87**
	Ca							-	.26*	.20	.13	.61**	.39**		- .25*	.47**
	Mg								-	- .15	.23*	.06	.06		.17	- .13
	Fe									-	- .20	.63**	.29*		- .45**	.66**
	Cu										-	.20	.02		- .11	.15
	Mn											-	.45**		- .67**	.79**
	Zn												-		- .25*	.41**
	B															
Soil pH															-	- .64**
Soil EC																-

** Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed) n= 102

For B in shoot, values lower limit of quantitation

Appendix

Table B.31: Correlation coefficients (r) for the relation between concentration of REE, macro- and micro-nutrients for **oilseed rape** roots and shoots 66 days after sowing in (2006)

		La	**Ce**	**Pr**	**Nd**	**S**	**K**	**Ca**	**Mg**	**Fe**	**Cu**	**Mn**	**Zn**	**B**	**Soil pH**	**Soil EC**
								Roots of oilseed rape								
Roots of oilseed rape	**La**	-	.67**	.77**	.77**	.19	- .07	.01	- .15	- .27**	.12	.37**	.18	- .51**	.19*	.28**
	Ce		-	.92**	.91**	.38**	.01	.04	- .15	- .32**	.25*	.39**	.37**	- .52**	.23*	.39**
	Pr			-	1.00**	.36**	- .01	.11	- .12	- .38**	.23*	.47**	.36**	- .56**	.21*	.36**
	Nd				-	.36**	- .01	.11	- .12	- .37**	.22*	.47**	.35**	- .56**	.20*	.35**
	S					-	.66**	.35**	.24*	- .52**	.73**	.45**	.50**	.007	- .01	.27**
	K						-	.29**	.24*	- .49**	.29**	.19*	.29**	.07	- .01	.10
	Ca							-	.38**	- .31**	.37**	.63**	.52**	.07	- .01	- .38**
	Mg								-	.02	.22*	.03	.08	.39**	- .33**	- .30**
	Fe									-	- .29**	- .33**	- .36**	.36**	- .15	- .28**
	Cu										-	.44**	.59**	.24*	- .14	.18
	Mn											-	.51**	- .17	- .03	.06
	Zn												-	- .09	- .01	.13
	B													-	- .41**	- .30**
Soil pH															-	.15
Soil EC																-
								Shoots of oilseed rape								
Shoots of oilseed rape	**La**	-	.46**	.36	.59**	.16	- .17	- .008	- .16	- .16	.08	.25*	.09	.15	.14	.19
	Ce		-	.99**	.86**	.11	.001	- .03	- .18	- .28**	.20	.31**	.31**	.33**	.30**	.43**
	Pr			-	.99**	.03	.22	.09	- .19	- .56**	.14	.46*	.39	.33	.47*	.52**
	Nd				-	.29**	- .01	.06	- .15	- .37**	.20	.45**	.33**	.45**	.24*	.41**
	S					-	.66**	.35**	.24*	- .52**	.73**	.45**	.50**	.61**	.28**	.28**
	K						-	.29**	.24*	- .49**	.29**	.19*	.29**	.07	- .01	.10
	Ca							-	.38**	- .31**	.37**	.63**	.52**	.09	- .01	- .38**
	Mg								-	.03	.22*	.03	.08	.01	- .33**	- .30**
	Fe									-	- .29**	- .33**	- .36**	- .15	- .15	- .28**
	Cu										-	.44**	.59**	.23*	- .14	.18
	Mn											-	.51**	.39**	- .03	.06
	Zn												-	.38**	- .01	.13
	B													-	- .11	.25*
Soil pH															-	.15
Soil EC																-

** Correlation significant at the 0.01 level (2-tailed) * Correlation significant at the 0.05 level (2-tailed) n= 102

Appendix

Table B.32: Correlation coefficients (r) for the relation between concentration of REE, macro- and micro-nutrients for **maize** and **oilseed rape** 35 days after sowing (2006)

		La	**Ce**	**Pr**	**Nd**	**S**	**K**	**Ca**	**Mg**	**Fe**	**Cu**	**Mn**	**Zn**	**B**
								Roots of maize						
	La	.88**	.68**	.71**	.71**	- .09	- .13	- .02	.02	- .06	.15	.59**	- .08	.17
	Ce		.88**	.84**	.84**	.00	- .19*	.02	.09	.07	.08	.62**	- .09	.23
	Pr			.85**	.85**	.09	- .21	.36	.43	.29	.45	.79**	- 36	.05
	Nd				.92**	- .07	- .01	- .01	.01	.12	.05	.57**	- .09	.23
Shoots of maize	**S**					.14	.11	.43**	.42**	.09	.12	.54**	- .06	.22
	K						.34**	- .25*	- .26**	- .06	- .36**	- .42**	.29**	- .31*
	Ca							.66**	.47**	- .06	.31**	.65**	.24*	.26*
	Mg								.26**	- .09	.19*	.25*	.28**	.001
	Fe									.35**	.13	- .06	- .01	- .11
	Cu										.05	.34**	.07	.11
	Mn											.85**	.09	.19
	Zn												.32**	.22
	B													.14
								Roots of oilseed rape						
	La	.86**	.32**	.39**	.36**	.09	- .04	.06	.24*	.61**	.46**	.53**	.47**	- .05
	Ce		.91**	.87**	.86**	.07	.08	.06	.39**	- .06	- .03	.21	.09	- .08
	Pr			.93**	.93**	.03	.05	.11	.44**	.06	.02	.32**	.26*	- .06
	Nd				.93**	.05	.02	.09	.44**	.03	.02	.26*	.16	- .05
Shoots of oilseed rape	**S**					.11	.12	.18	.03	.01	.09	.25*	.22*	- .08
	K						.06	- .09	- .10	- .25*	- .14	- .12	- .06	- .09
	Ca							.03	.17	.19	.13	.29*	.34**	.07
	Mg								.02	.13	.003	.14	.23*	- .02
	Fe									.07	.18	.28**	.24*	- .16
	Cu										.24*	- .09	.19	.43**
	Mn											.44**	.44**	- .16
	Zn												.37**	.01
	B													- .09

** Correlation significant at the 0.01 level (2-tailed)   * Correlation significant at the 0.05 level (2-tailed)   n= 102

Appendix

Table B.33: Correlation coefficients (r) for the relation between concentration of REE, macro- and micro-nutrients for **maize** roots and shoots 35 days after sowing (2006)

		La	**Ce**	**Pr**	**Nd**	**S**	**K**	**Ca**	**Mg**	**Fe**	**Cu**	**Mn**	**Zn**	**B**
								Roots of maize						
Roots of maize	**La**	-	.77**	.79**	.79**	.04	- .02	.13	.09	- .06	.25*	.72**	- .06	.25
	Ce		-	.98**	.98**	- .02	- .15	.13	.09	.05	.013	.71**	- .05	.27*
	Pr			-	1.00**	- .06	- .17	.09	.04	.06	.11	.65**	- .06	.27*
	Nd				-	-.06	- .17	.09	.04	.06	.011	.65**	- .06	.27*
	S					-	.54**	.49**	.36**	.01	.25*	.31**	.35**	.21
	K						-	.35**	.21*	- .04	.16	.14	.31**	- .06
	Ca							-	.65**	.04	.28**	.44**	.18	.08
	Mg								-	- .02	.31**	.46**	.03	.15
	Fe									-	.31**	.13	.001	.28*
	Cu										-	.46**	.05	.28*
	Mn											-	.02	.26*
	Zn												-	- .09
	B													-
								Shoots of maize						
Shoots of maize	**La**	-	.62**	.94**	.72**	.25*	- .43**	.36**	.06	- .07	.33**	.48**	.19	.13
	Ce		-	.99**	.93**	.53**	- .38**	.30**	- .12	- .12	.49**	.53**	.22*	.22*
	Pr			-		.61**	- .85**	.57*	.13	- .29	.43	.67**	.44	- .44
	Nd				-	.55**	- .44**	.32**	- .14	- .12	.52**	.45**	.27**	.27**
	S					-	- .26**	.47**	- .14	- .08	.38**	.47**	.09	.21*
	K						-	- .34**	.02	.01	- .16	- .42**	- .19	.19
	Ca							-	.39**	- .14	.28**	.64**	.33**	.34**
	Mg								-	- .04	- .12	.34**	.22*	- .03
	Fe									-	- .07	- .14	- .09	.00
	Cu										-	.22*	.18	.29**
	Mn											-	.30**	.18
	Zn												-	.12
	B													-

** Correlation significant at the 0.01 level (2-tailed)   * Correlation significant at the 0.05 level (2-tailed)   n= 102

Appendix

Table B.34: Correlation coefficients (r) for the relation between concentration of REE, macro- and micro-nutrients for **oilseed rape** roots and shoots 35 days after sowing (2006)

		La	Ce	Pr	Nd	S	K	Ca	Mg	Fe	Cu	Mn	Zn	B
								Roots of oilseed rape						
Roots of oilseed rape	**La**	-	.60**	.65**	.64**	.16	- .06	.03	.35**	.52**	.34**	.53**	.42**	- .02
	Ce		-	.97**	.97**	.16	- .006	.08	.44**	.05	.03	.29**	.17	- .04
	Pr			-	1.00**	.24*	- .06	.05	.45**	.06	.03	.28**	.15	- .02
	Nd				-	.22*	- .07	.08	.45**	.08	.05	.30**	.18	- .02
	S					-	- .08	.08	.12	.04	.01	.23*	.01	.27*
	K						-	.38**	.02	- .25*	- .02	.11	- .09	- .16
	Ca							-	.13	.11	.04	.61**	.16	- .22
	Mg								-	.09	.05	.32**	.14	.002
	Fe									-	.69**	.57**	.62**	.28*
	Cu										-	.47**	.55**	.13
	Mn											-	.55**	- .09
	Zn												-	- .01
	B													-
								Shoots of oilseed rape						
Shoots of oilseed rape	**La**	-	.32**	.51**	.39**	.09	- .11	.18	.09	.26*	.11	.43**	.22	.24*
	Ce		-	.94**	.94**	.07	.02	.15	.05	.51**	- .26*	.11	.12	- .01
	Pr			-	1.00**	.03	- .14	.13	- .05	.57**	- .25*	.17	.11	- .09
	Nd				-	.05	- .14	.16	- .03	.58**	- .20	.17	.11	- .09
	S					-	.67**	.69**	.69**	.38**	.04	.53**	.49**	.61**
	K						-	.49**	.63**	.05	.02	.29**	.44**	.57**
	Ca							-	.79**	.22*	.22*	.66**	.74**	.77**
	Mg								-	.11	.13	.59**	.69**	.72**
	Fe									-	- .20	.26*	.13	- .06
	Cu										-	.14	.39**	.24*
	Mn											-	.58**	.57**
	Zn												-	.66**
	B													-

** Correlation significant at the 0.01 level (2-tailed) * Correlation significant at the 0.05 level (2-tailed) n= 102

Appendix

Table B.35: Correlation coefficients (r) for the relation between **uptake** of REE, macro- and micro-nutrients for **maize** roots and shoots and soil pH and EC 66 days after sowing (2006)

		La	Ce	Pr	Nd	S	K	Ca	Mg	Fe	Cu	Mn	Zn	B	Soil pH	Soil EC
									Roots of maize							
	La	-	.27**	.51**	.51**	- .29**	- .39**	- .29**	- .54**	- .04	- .10	- .29**	- .24*	- .11	- .01	.28**
	Ce		-	.68**	.68**	- .15	- .18	- .28**	- .14	.13	- .27**	- .14	- .17	- .05	.06	.31**
	Pr			-	.99**	- .46**	- .56**	- .55**	- .39**	- .09	- .39**	- .26**	- .19*	- .37**	- .20*	.64**
	Nd				-	- .44**	- .55**	- .54**	- .37**	- .06	- .39**	- .24*	- .19	- .35**	- .18	.62**
	S					-	.78**	.86**	.77**	.68**	.57**	.57**	.38**	.63**	.53**	- .78**
Roots of maize	**K**						-	.74**	.65**	.37**	.54**	.39**	.22*	.73**	.44**	- .71**
	Ca							-	.75**	.53**	.49**	.55**	.46**	.58**	.53**	- .83**
	Mg								-	.56**	.31**	.68**	.35**	.78**	.28**	- .60**
	Fe									-	.28**	.49**	.36**	.63**	.52**	- .56**
	Cu										-	.04	.09	.41**	.48**	- .61**
	Mn											-	.34**	.38**	- .004	- .39**
	Zn												-	.79**	.24*	- .34**
	B													-	.53**	- .81**
Soil pH															-	- .64**
Soil EC																-
									Shoots of maize							
	La	-	.30*	.92**	.97**	- .32*	- .20	- .29*	- .59**	- .12	- .19	- .23	- .13	.81	.05	.33*
	Ce		-	.91**	.76**	- .07	.05	- .25*	- .36**	- .03	- .13	.14	- .05	.74	- .09	.42**
	Pr			-	.91**	- .42	- .37	- .43	- .60*	- .58	- .46	- .28	.07		.32	.42
	Nd				-	- .35*	- .14	- .58**	- .65**	- .11	- .53**	.003	- .14	.79	- .26	.63**
	S					-	.61**	.39**	.65**	.36**	.67**	.48**	.41**		.14	- .46**
Shoots of maize	**K**						-	.16	.24*	.25*	.30*	.45**	.14		- .32**	.08
	Ca							-	.47**	.18	.45**	.29*	.43**		.28*	- .50**
	Mg								-	.09	.66**	.03	.45**		.51**	- .77**
	Fe									-	- .12	.57**	.19		- .14	- .02
	Cu										-	.040	.34**	- .99	.37**	- .65**
	Mn											-	.27*	.94	- .37**	.14
	Zn												-	.73	.01	- .38**
	B													-	.41	.86
Soil pH															-	- .64**
Soil EC																-

** Correlation significant at the 0.01 level (2-tailed)   * Correlation significant at the 0.05 level (2-tailed)   n= 102

For B in shoot, absent values are lower limit of quantitation

Appendix

Table B.36: Correlation coefficients (r) for the relation between **uptake** of REE, macro- and micro-nutrients for **oilseed rape** roots and shoots and soil pH and EC 66 days after sowing (2006)

		La	Ce	Pr	Nd	S	K	Ca	Mg	Fe	Cu	Mn	Zn	B	Soil pH	Soil EC
		Roots of oilseed rape														
Roots of oilseed rape	**La**	-	.56**	.67**	.67**	.06	- .06	- .18	- .02	- .04	.01	.14	- .01	- .12	.17	.21*
	Ce		-	.90**	.89**	.10	- .09	- .09	- .07	- .11	.01	.12	.11	- .19*	.20*	.29**
	Pr			-	.99**	.12	- .09	- .03	- .03	- .12	.03	.21*	.12	- .18	.18	.28**
	Nd				-	.14	- .07	- .02	- .01	- .09	.05	.22*	.13	- .15	.17	.27**
	S					-	.68**	.53**	.77**	.57**	.81**	.64**	.61**	.72**	.01	- .48**
	K						-		.78**	.59**	.66**	.55**	.58**	.76**	.05	- .31**
	Ca							-	.59**	.35**	.56**	.76**	.65**	.52**	.004	- .62**
	Mg								-	.81**	.74**	.65**	.65**	.89**	- .08	- .49**
	Fe									-	.67**	.55**	.55**	.89**	- .03	- .40**
	Cu										-	.69**	.69**	.78**	- .08	- .35**
	Mn											-	.64**	.63**	- .02	- .37**
	Zn												-	.62**	.01	- .36**
	B													-	- .09	- .48**
Soil pH															-	.15
Soil EC																-
		Shoots of oilseed rape														
Shoots of oilseed rape	**La**	-	.49**	.39*	.62**	.12	- .03	- .05	- .09	- .08	.08	.37**	- .05	.01	.11	.21*
	Ce		-	.99**	.86**	.09	- .06	- .05	- .09	- .02	.11	.42**	- .11	.18	.25*	.43**
	Pr			-	.99*	- .03	.11	.14	.06	- .01	.17	.45*	- .36	.16	.34	.55**
	Nd				-	.23*	.04	. 01	- .02	- .08	.15	.55**	- .11	.31**	.18	.42**
	S					-	.68**	.48**	.54**	.12	.49**	.65**	.13	.73**	- .20	.19
	K						-	.59**	.74**	.24*	.58**	.49**	.19	.52**	- .16	.02
	Ca							-	.82**	.14	.61**	.45**	.32**	.59**	- .17	- .23*
	Mg								-	.34**	.60**	.40**	.23**	.47**	- .13	- .26*
	Fe									-	.18	.03	.16	- .13	.16	- .05
	Cu										-	.53**	.05	.52**	.03	.03
	Mn											-	.16	.68**	- .01	.27**
	Zn												-	.12	- .04	.05
	B													-	- .34*	.15
Soil pH															-	.15
Soil EC																-

** Correlation significant at the 0.01 level (2-tailed) * Correlation significant at the 0.05 level (2-tailed) n= 102

For B in shoot, values lower limit of quantitation

Appendix

Table B.37: Correlation coefficients (r) for the relation between **uptake** of REE, macro- and micro-nutrients for **maize** and **oilseed rape** 66 days after sowing (2006)

		La	Ce	Pr	Nd	S	K	Ca	Mg	Fe	Cu	Mn	Zn	B
								Roots of maize						
Shoots of maize	**La**	.89**	.39**	.74**	.74**	- .55**	- .57**	- .54**	- .64**	- .29*	- .31*	- .39**	- .30*	- .37**
	Ce		.77**	.68**	.67**	- .35**	- .33**	- .39**	- .28*	- .12	- .33**	- .06	- .24*	- .32**
	Pr			.68*	.67*	- .69*	- .53	- .67	- .54	- .54	- .64*	- .31	- .36	- .52
	Nd				.88**	- .69**	- .63**	- .64**	- .62**	- .42*	- .60**	- .46**	- .31	- .59**
	S					.41**	.35**	- .09	.23*	.032**	- .60**	- .46**	- .31	- .59**
	K						.13	- .09	.23	.03	- .09	.23*	- .02	.001
	Ca							.49**	.42**	.51**	.28**	.41**	.30**	- .29*
	Mg								.55**	.58**	.50**	.37**	.33**	.74**
	Fe									.23*	- .18	.28*	.32**	.09
	Cu										.39**	.33**	.13	.49**
	Mn											.26*	.12	- .19
	Zn												.15	.36**
	B													- 1.00**
								Roots of oilseed rape						
Shoots of oilseed rape	**La**	.81**	.39**	.73**	.47**	- .34*	- .32**	- .18	- .24*	- .23*	- .22*	- .02	- .18	- .34**
	Ce		.85**	.77**	.72**	.11	- .29**	- .25*	- .32**	- .31**	- .22*	- .08	- .10	- .45**
	Pr			.88**	.76**	.05	- .11	- .19	- .19	- .36	- .17	.18	.04	- .44*
	Nd				.87**	- .08	- .26*	- .17	- .27*	- .33**	- .19	.08	- .06	- .44**
	S					.21*	.06	.15	- .04	- .09	.02	.29**	.09	- .08
	K						.23**	.20	.13	.07	.08	.33**	.09	.11
	Ca							.44**	.34*	.28**	.36**	.53**	.36**	.36**
	Mg								.45**	.34**	.44**	.57**	.39**	.42**
	Fe									.06	.09	- .02	.03	.11
	Cu										.15	.39**	.26*	.19
	Mn											.38**	.14	- .13
	Zn												.04	- .02
	B													- .04

** Correlation significant at the 0.01 level (2-tailed)   * Correlation significant at the 0.05 level (2-tailed)   n= 102

Appendix

Table B.38: Influence of graded REE applications on mean of transfer factors (**TF,** µg µg^{-1}) of individual and total of REE for **roots of maize** 66 days after sowing (2006)

Application rate (µg g^{-1})	Individual TF (µg µg^{-1}) for roots of maize				
	La	**Ce**	**Pr**	**Nd**	**Total TF_{roots}**
Lanthanum					
0	4.24 c	11.04 c	4.47 c	4.67 c	6.39 c
1.0	2.01 b	4.96 b	2.01 b	2.09 b	4.24 b
10	0.81 a	0.95 a	0.39 a	0.41 a	1.68 a
50	0.41 a	0.19 a	0.08 a	0.08 a	0.62 a
100	0.54 a	0.11 a	0.05 a	0.05 a	0.66 a
Cerium					
0	4.24 c	11.04 c	4.47 c	4.67 c	6.39 d
0.8	1.98 b	5.51 b	2.18 b	2.26 b	4.80 c
8.0	0.35 a	1.46 a	0.39 a	0.40 a	1.94 b
40	0.09 a	0.69 a	0.09 a	0.10 a	0.87 a
80	0.04 a	0.63 a	0.05 a	0.05 a	0.72 a
REE-fertilizer					
0	4.24 c	11.04 c	4.47 c	4.67 c	6.39 c
2.7	2.36 b	6.14 b	2.54 b	2.59 b	3.56 b
27	0.92 a	2.24 a	0.91 a	0.89 a	1.29 a
135	0.67 a	1.42 a	0.57 a	0.53 a	0.85 a
270	1.19 a	2.23 a	0.88 a	0.80 a	1.38 a
Calcium					
0	4.24 d	11.04 d	4.47 d	4.67 d	6.39 ab
1.0	2.00 c	5.38 c	2.20 c	2.27 c	6.18 a
10	0.42 b	1.11 b	0.46 b	0.48 b	7.11 ab
50	0.11 a	0.29 a	0.12 a	0.12 a	8.49 b
100	0.05 a	0.12 a	0.05 a	0.05 a	7.25 ab

Table B.39: Influence of graded REE applications on mean of transfer factors (**TF,** µg µg^{-1}) of individual and total of REE for **shoots of maize** 66 days after sowing (2006)

Application rate (µg g^{-1})	Individual TF (µg µg^{-1}) for shoots of maize				
	La	**Ce**	**Pr**	**Nd**	**Total TF_{shoots}**
Lanthanum					
0	0.096	0.283	-----*	0.084	0.142
1.0	0.035	0.060	-----*	-----	0.045
10	0.015	0.018	-----*	0.051	0.029
50	----**	-----**	-----**	-----**	-----**
100	0.010	0.002	------*	-----*	0.011
Cerium					
0	0.096 c	0.283	-----*	0.084 c	0.142 b
0.8	0.047 b	0.103	-----*	0.048 b	0.028 a
8.0	0.005 a	0.023	-----*	0.009 a	0.026 a
40	0.001 a	0.007	-----*	0.002 a	0.009 a
80	0.001 a	0.007	------*	0.001 a	0.007 a
REE-fertilizer					
0	0.096 b	0.283 b	-----*	0.084	0.142 c
2.7	0.031 a	0.054 a	-----*	0.047	0.026 b
27	0.014 a	0.027 a	-----*	0.010	0.016 ab
135	0.008 a	0.013 a	0.007	0.005	0.008 a
270	0.017 a	0.022 a	0.009	0.008	0.015 ab
Calcium					
0	0.096	0.283 c	-----*	0.084	0.142 b
1.0	0.058	0.063 b	-----*	-----*	0.043 a
10	0.008	0.014 a	-----*	0.011	0.066 ab
50	0.001	0.002 a	-----*	----*	0.028 a
100	0.001	0.001 a	------*	0.001	0.055 ab

* < Lower limit of quantitation   ** no data

For values, which have no letters ANOVA could not be run because of limited cases

Appendix

Table B.40: Influence of graded REE applications on mean of transfer factors (**TF,** µg µg^{-1}) of individual and total of REE for **roots of oilseed rape** 66 days after sowing (2006)

Application rate (µg g^{-1})	Individual TF (µg µg^{-1}) for roots of oilseed rape La	Ce	Pr	Nd	Total TF_{roots}
Lanthanum					
0	9.54 c	23.92 c	9.44 c	9.68 c	13.83 b
1.0	5.87 b	12.86 b	5.16 b	5.31 b	11.30 b
10	2.13 a	2.03 a	0.80 a	0.83 a	3.89 a
50	1.48 a	0.44 a	0.17 a	0.17 a	1.92 a
100	1.25 a	0.23 a	0.09 a	0.09 a	1.49 a
Cerium					
0	9.54 c	23.92 c	9.44 c	9.68 c	13.83 c
0.8	4.24 b	11.44 b	4.21 b	4.35 b	9.88 b
8.0	0.79 a	2.94 a	0.77 a	0.79 a	3.96 a
40	0.18 a	1.57 a	0.18 a	0.18 a	1.96 a
80	0.09 a	1.46 a	0.09 a	0.09 a	1.64 a
REE-fertilizer					
0	9.54 c	23.92 c	9.44 c	9.68 c	13.83 c
2.7	5.60 b	13.12 b	5.25 b	5.25 b	7.71 b
27	2.72 a	5.74 a	2.29 a	2.12 a	3.43 a
135	2.04 a	3.96 a	1.54 a	1.36 a	2.39 a
270	1.62 a	2.92 a	1.08 a	0.95 a	1.79 a
Calcium					
0	9.54 c	23.92 c	9.44 c	9.68 c	13.83 a
1.0	4.20 b	10.49 b	4.22 b	4.38 b	12.22 a
10	0.72 a	1.77 a	0.71 a	0.74 a	11.38 a
50	0.17 a	0.44 a	0.18 a	0.18 a	12.95 a
100	0.08 a	0.19 a	0.08 a	0.08 a	11.72 a

* no data   Values, which have not letters mean a few of data and not complete statistical analysis

Table B.41: Influence of graded REE applications on mean of transfer factors (**TF,** µg µg^{-1}) of individual and total of REE for **shoots of oilseed rape** 66 days after sowing (2006)

Application rate (µg g^{-1})	Individual TF (µg µg^{-1}) for shoots of oilseed rape La	Ce	Pr	Nd	Total TF_{shoots}
Lanthanum					
0	0.225 a	0.468 a	0.511	0.182 a	0.277
1.0	0.129 a	0.195 a	0.117	0.079 a	0.186
10	0.087 a	0.049 a	0.030	0.020 a	0.124
50	0.077 a	0.014 a	0.011	0.005 a	0.089
100	0.066 a	0.008 a	0.005	0.003 a	0.075
Cerium					
0	0.225 b	0.468 b	----*	0.182 b	0.277 b
0.8	0.125 ab	0.222 ab	----*	0.091 ab	0.200 ab
8.0	0.016 a	0.075 a	-----*	0.012 a	0.087 ab
40	0.004 a	0.049 a	----*	0.003 a	0.054 a
80	0.002 a	0.042 a	----*	0.002 a	0.044 a
REE-fertilizer					
0	0.225 b	0.468 b	0.511	0.182 b	0.277 a
2.7	0.116 ab	0.222 ab	0.176	0.087 ab	0.134 ab
27	0.072 a	0.129 a	0.053	0.046 a	0.080 a
135	0.049 a	0.092 a	0.040	0.038 a	0.058 a
270	0.037 a	0.070 a	0.031	0.029 a	0.044 a
Calcium					
0	0.225 b	0.468 b	----*	0.182	0.277 a
1.0	0.067 a	0.119 a	----*	0.048	0.141 a
10	0.014 a	0.027 a	-----*	0.011	0.174 a
50	0.003 a	0.005 a	----*	0.002	0.158 a
100	0.001 a	0.003 a	----*	0.001	0.151 a

* < Lower limit of quantitation

For values, which have no letters ANOVA could not be run because of limited cases

Table B.42: Influence of graded REE applications on mean of α-tocopherol (µg g^{-1} DW) and total chlorophyll (µmol g^{-1} DW) in leaf discs of maize and oilseed rape 66 days after sowing (2005)

Application rate (µg g^{-1})	Maize		Oilseed rape	
	α-Tocopherol (µg g^{-1} DW)	**Total chlorophyll (µmol g^{-1} DW)**	**α-Tocopherol (µg g^{-1} DW)**	**Total chlorophyll (µmol g^{-1} DW)**
Lanthanum				
0	59.4 a	7.5 a	194.2 a	13.8 a
1.0	74.4 a	6.7 a	193.2 a	12.9 a
10	61.7 a	7.4 a	178.6 a	11.4 a
50	66.3 a	8.4 a	214.5 a	12.3 a
100	82.6 a	6.1 a	151.6 a	11.5 a
Cerium				
0	59.4	7.5	----*	----*
0.8	103.1	7.8	----*	----*
8.0	-----*	----*	----*	----*
40	-----*	----*	----*	----*
80	-----*	----*	----*	----*
REE fertilizer				
0	59.4 a	7.5 a	194.2 a	13.8 a
2.7	86.6 a	7.3 a	184.1 a	12.2 a
27	64.9 a	7.3 a	189.7 a	13.6 a
135	73.9 a	6.9 a	233.8 a	11.3 a
270	95.1 a	8.5 a	248.3 a	10.2 a
Calcium				
0	59.4	7.5	----*	----*
9.83	162.8	9.8	----*	----*
98.3	52.7	6.8	----*	----*
491.5	do	do	do	do
983	do	do	do	do
Copper				
0	59.4	7.5	194.2	13.8
4.3	39.2	6.1	201.4	11.0
43	51.6	6.7	236.0	7.9
215	do	do	541.4	7.3
430	do	do	do	do

do, all plants died off * no data
Values followed by the same letters are not significantly different by Tukey's test at 0.05 level

Table B.43: Correlation coefficients (r) for the relation between total chlorophyll and α–tocopherol content in maize roots and REE concentrations in roots and shoots of maize and oilseed rape and soil pH and soil EC 33 days after sowing (2005) (n= 84)

	Roots				Shoots					
	La	**Ce**	**La**	**Ce**	**Pr**	**Nd**	**Pr**	**Nd**	**Soil pH**	**Soil EC**
	Maize									
α–tocopherol	0.05	0.04	0.06	0.06	0.18	0.23	0.04	0.04	- 0.01	0.16
Total chlorophyll	0.08	0.12	0.07	0.15	0.85*	0.38	0.12	0.12	0.10	0.12
	Oilseed rape									
α–tocopherol	0.14	0.25	0.25	0.25	0.02	0.23	0.50	0.23	0.17	0.04
Total chlorophyll	- 0.19	- 0.20	- 0.21	- 0.21	- 0.13	- 0.20	- 0.52	- 0.20	0.20	- 0.02

* Correlation significant at the 0.01 level (2-tailed). * Correlation significant at the 0.05 level (2-tailed).

Appendix

Table C.1 (a): Analytical data of biomass production, germination rate (GR), plant height and soil microbial counts (Colony Forming Unit, CFU) of maize 66 days after sowing (2005)

Treatment	Biomass (g pot^{-1})			GR (%)	Plant height (cm)	Soil microbial counts (CFU)		
	Roots	Shoots	Total			Bacteria	Actino-mycetes	Fungi
Control	1.92	4.54	6.46	100	56	5080662	2409386	4975906
Control	8.37	26.88	35.25	100	81	8894230	1869658	1228632
Control	1.80	5.70	7.50	83.3	69	4956760	1713773	1397384
Control	3.36	9.42	12.78	83.3	61	7705210	1310409	1205577
La1	1.28	6.28	7.56	100	73	5332496	862609	1359263
La1	5.64	19.98	25.62	83.3	72	5397396	1746216	1481638
La1	1.26	5.62	6.88	83.3	65	62916358	2537802	845934
La1	3.15	10.92	14.07	100	63	66945606	1412133	862970
La2	0.15	0.73	0.88	83.3	do*	5605853	12896	115801
La2	1.74	5.42	7.16	83.3	64	53665871	21777	147775
La2	0.38	1.41	1.79	83.3	0.0	6909415	2075451	998318
La2	2.58	9.30	11.88	100	77	6178310	2450469	964546
La3	4.83	21.00	25.83	83.3	70	71729957	2663502	1054852
La3	1.54	6.08	7.62	100	70	76789107	2137428	870804
La3	5.43	23.10	28.53	100	82	66985394	3414941	1471051
La3	2.36	9.18	11.54	83.3	73	66731245	3363470	1614465
La4	4.83	15.99	20.82	100	70	59000952	3677637	1534553
La4	0.71	2.45	3.16	83.3	80	4689605	1813659	300549
La4	7.20	27.18	34.38	100	86	63809422	4865468	1621822
La4	3.00	8.76	11.76	100	55	4940293	4015639	1109584
Ce1	4.65	15.84	20.49	100	65	61393339	2345067	1554595
Ce1	0.01	0.86	0.87	66.7	57	4426401	2462022	628601
Ce1	0.86	5.50	6.36	100	60	812705832	4568150	1115478
Ce1	1.12	2.58	3.70	100	55	692901724	3226488	819845
Ce2	0.32	1.05	1.37	100	62	720852486	3813205	888006
Ce2	2.18	8.00	10.18	100	70	67146029	2590673	872369
Ce2	do	do	do	83.3	do	49604221	1345646	242744
Ce2	3.90	12.09	15.99	100	61	64480471	2289714	1658069
Ce3	0.32	1.12	1.44	100	68	4847207	3266596	284510
Ce3	8.61	25.83	34.44	83.3	79	5743525	2349624	2088554
Ce3	7.20	19.98	27.18	83.3	78	58127301	1972646	1104681
Ce3	1.53	20.07	21.6	83.3	78	60892028	1792492	1159848
Ce4	4.86	11.34	16.20	100	59	5431376	809484	1932316
Ce4	6.57	22.11	28.68	100	72	60218786	4181129	1735563
Ce4	3.60	10.28	13.88	83.3	75	4564423	1043296	1538862
Ce4	1.18	3.96	5.14	100	77	4826356	603294	1049207
Ca1	1.74	2.42	4.16	83.3	48	4532117	217436	1074085
Ca1	6.18	19.02	25.2	100	73	4264055	152663	1289745
Ca1	do	do	do	83.3	do	4535327	1034373	1007850
Ca1	do	do	do	83.3	57	51565281	1256412	1361114
Ca2	do	do	do	100	do	44685351	898995	216816
Ca2	do	do	do	83.3	60	54936305	1645435	530785
Ca2	3.28	8.62	11.90	100	70	75500688	6251986	1430539
Ca2	1.12	1.95	3.07	83.3	70	5250997	2441713	1207729
Ca3	do	do	do	50	do	520508	1119092	189985
Ca3	do	do	do	83.3	do	522466	1358411	159352
Ca3	do	do	do	50	do	521920	1148225	96555
Ca3	do	do	do	66.7	do	5193186	2700457	85687
Ca4	do	do	do	0.0	do	52012899	1040258	20545
Ca4	do	do	do	33.3	do	47982155	1244942	31901
Ca4	do	do	do	16.7	do	607191672	1761118	27862
Ca4	do	do	do	16.7	do	51111344	1651289	68148
REE1	5.19	13.38	18.57	83.3	67	64392346	2207737	946173
REE1	9.96	28.08	38.04	100	73	81384323	2028023	1975347
REE1	4.44	9.51	13.95	83.3	59	5042546	1996008	551528
REE1	7.53	21.90	29.43	100	72	27431947	2136526	2004642
REE2	2.14	4.28	6.42	83.3	54	5579058	1084082	951877
REE2	1.74	6.36	8.10	83.3	80	54255769	2699555	899851
REE2	0.88	2.10	2.98	66.7	70	4407929	2634324	1121544

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REE2	0.84	1.91	2.75	100	64	4143501	2202874	1075212
REE3	0.72	1.59	2.31	100	68	4825440	3032380	896529
REE3	5.88	15.12	21.00	100	66	3985851	2270087	1319818
REE3	3.10	9.76	12.86	83.3	76	6931216	1613756	1455026
REE3	0.97	2.35	3.32	100	73	7412898	2620989	1932648
REE4	do	do	do	66.7	do	5630986	3052310	257867
REE4	2.64	8.67	11.31	100	8	5530856	2699269	793902
REE4	4.68	14.07	18.75	83.3	79	5123379	2849226	1437683
REE4	6.27	17.52	23.79	100	69	4831045	2191129	791974
Cu1	do	do	do	66.7	46	4119597	2772308	145092
Cu1	7.32	17.7	25.02	100	62	4179810	2865404	578338
Cu1	6.54	16.83	23.37	100	70	3635109	1140946	1034812
Cu1	3.68	11.82	15.50	83.3	83	5532027	3361567	1058761
Cu2	9.63	23.43	33.06	83.3	72	5997931	1990692	1758014
Cu2	0.08	0.28	0.36	83.3	61	5151929	3259383	262853
Cu2	5.64	18.9	24.54	100	70	4834767	3692487	1434491
Cu2	0.09	0.44	0.53	100	57	3999579	3183875	334175
Cu3	do	do	do	16.7	do	752621	2439530	168691
Cu3	do	do	do	66.7	do	465225	3196798	127352
Cu3	do	do	do	66.7	do	648542	1971567	236069
Cu3	do	do	do	66.7	do	5305	2848630	107150
Cu4	do	do	do	16.7	do	269633	12565	371727
Cu4	do	do	do	0.0	do	3790651	1751542	31109
Cu4	do	do	do	16.7	do	2137866	1772864	172072
Cu4	do	do	do	16.7	do	2356048	1786454	30033

*do, all plants died off

Appendix

Table C.1 (b): Analytical data of biomass production, germination rate (GR), plant height and soil microbial counts (Colony Forming Unit, CFU) of oilseed rape 66 days after sowing (2005)

Treatment	**Biomass (g pot^{-1})**			**GR (%)**	**Plant height (cm)**	**Soil microbial counts (CFU)**		
	Roots	**Shoots**	**Total**			**Bacteria**	**Actino-mycetes**	**Fungi**
Control	1.28	9.48	10.76	60	35	5639890	3610584	1818469
Control	1.83	14.52	16.35	60	24	5430711	3049759	1631888
Control	0.05	0.79	0.84	60	17	5259504	4325074	2055745
Control	0.90	11.25	12.15	90	22	4996279	3853513	2099500
La1	2.25	14.22	16.47	50	27	6479140	1316898	2396755
La1	2.84	22.92	25.76	60	41	4943653	2073144	1754199
La1	1.44	18.30	19.74	70	24	5042998	1619067	1486357
La1	1.11	12.42	13.53	50	26	4063753	2269368	949968
La2	2.12	22.60	24.72	70	44	47089947	3439153	1719576
La2	0.43	2.33	2.76	30	25	43762522	2979015	553622
La2	2.44	18.16	20.60	60	25	66020658	3327654	1118091
La2	3.44	18.76	22.20	90	32	48152826	2262919	1841911
La3	do*	do	do	70	39	5681818	3866792	1210016
La3	2.56	19.96	22.52	90	31	4650671	3250185	1056970
La3	1.88	16.72	18.60	60	26	4667229	2399535	1002004
La3	2.64	17.76	20.40	90	25	4878048	3499469	1352067
La4	0.39	8.82	9.21	90	20	4461024	4408849	939163
La4	2.40	19.56	21.96	60	25	4318157	2745495	1546007
La4	0.92	15.36	16.28	70	24	5667973	3708019	8210615
La4	0.44	2.72	3.16	30	19	4766893	3509690	8119434
Ce1	3.24	19.84	23.08	70	27	4473629	3060904	2406864
Ce1	2.88	19.64	22.52	70	25	5211102	2818249	797617
Ce1	0.78	12.63	13.41	50	31	4447268	4103134	979457
Ce1	2.88	16.12	19.00	60	25	4847645	2956531	197102
Ce2	0.18	6.44	6.62	40	29	4840576	4472271	1157529
Ce2	1.02	39.81	40.83	40	26	4905080	1802948	954502
Ce2	0.94	26.38	27.32	40	26	4400469	3173671	1306806
Ce2	3.20	57.08	60.28	80	23	4970022	2524455	1393709
Ce3	2.25	14.01	16.26	70	36	704298831	4382303	1695534
Ce3	1.56	11.49	13.05	80	22	679678409	3014915	1137205
Ce3	1.12	8.1	9.22	40	27	673961306	4228776	977904
Ce3	1.52	19.96	21.48	70	40	658376005	3135123	1332427
Ce4	2.92	19.52	22.44	80	19	515138772	4310344	2181455
Ce4	1.56	18.24	19.80	70	44	52562070	2852614	1030110
Ce4	2.80	19.08	21.88	80	24	44402156	3938048	2035098
Ce4	0.88	16.40	17.28	70	25	50977506	2496321	1497792
Ca1	3.36	21.88	25.24	50	23	51794496	3740713	1569530
Ca1	1.74	15.03	16.77	40	24	60638297	2180851	1648936
Ca1	3.76	22.88	26.64	80	26	60266001	2701579	2337905
Ca1	1.44	14.31	15.75	50	23	63719320	1861757	1048877
Ca2	1.50	12.24	13.74	30	21	725475764	4205656	1103984
Ca2	0.06	8.16	8.22	30	24	526703887	3107552	1079743
Ca2	1.60	15.52	17.12	70	24	574561863	3174519	8395424
Ca2	0.57	4.80	5.37	80	18	689058897	2462796	523999
Ca3	do	do	do	30	14	35485227	3417096	210282
Ca3	0.69	2.07	2.76	40	12	38069733	1916614	283553
Ca3	0.19	0.56	0.75	10	15	34027850	1413464	180609
Ca3	do	do	do	10	do	40752351	470219	151515
Ca4	do	do	do	0.0	do	430393198	1248671	27364
Ca4	do	do	do	0.0	do	23649358	3179524	107736
Ca4	do	do	do	0.0	do	5759162	1596858	27225
Ca4	do	do	do	0.0	do	3938856	1747704	93906
REE1	3.76	21.08	24.84	50	do	5227938	2326432	2065035
REE1	1.48	19.28	20.76	60	23	5364806	2601931	1046137
REE1	1.20	12.54	13.74	40	26	5314625	3507653	930059
REE1	0.72	21.24	21.96	70	23	5243288	3329488	1966233
REE2	3.40	20.24	23.64	60	32	31041318	2321577	2086811
REE2	4.00	18.96	22.96	70	22	28723290	3758187	1422742

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REE2	0.87	10.89	11.76	60	28	29914529	427350	1495726
REE2	2.76	22.56	25.32	100	25	24010554	3535620	1767810
REE3	1.41	11.82	13.23	60	32	44166840	4338281	1202174
REE3	3.36	20.72	24.08	80	22	41639974	3496690	1628229
REE3	2.36	17.56	19.92	80	24	23923445	2977139	1967038
REE3	2.52	19.08	21.60	90	23	25927089	3090299	1545149
REE4	do	do	do	0.0	do	3317659	2089864	444096
REE4	0.40	5.02	5.42	20	24	29573072	3279922	1828153
REE4	0.29	0.34	0.63	10	19	5337888	352300	314935
REE4	0.48	5.48	5.96	30	22	5306728	4829123	167162
Cu1	1.11	10.86	11.97	40	36	5253756	4491961	919407
Cu1	0.54	2.92	3.46	50	15	5351600	3451782	454886
Cu1	2.61	14.1	16.71	80	22	5363655	3835013	1609096
Cu1	0.58	5.74	6.32	60	26	5260389	2788006	473435
Cu2	0.06	3.68	3.74	40	16	5231767	3034425	837082
Cu2	0.25	do	0.25	50	do	2296450	1122129	195720
Cu2	0.10	2.06	2.16	50	17	4763678	4683840	239514
Cu2	do	do	do	30	19	3962006	3043660	309613
Cu3	do	do	do	10	13	3696272	2772204	306262
Cu3	do	do	do	0.0	do	2644532	3246753	308965
Cu3	do	do	do	10	do	3428960	1963145	287928
Cu3	do	do	do	0.0	do	1712684	1479136	145318
Cu4	do	do	do	0.0	do	879007	64632	211995
Cu4	do	do	do	0.0	do	885047	104123	364431
Cu4	do	do	do	0.0	do	2033580	432787	1694650
Cu4	do	do	do	0.0	do	1299106	192267	519642

*do, all plants died off

Appendix

Table C.2 (a): Analytical data of biomass production, germination rate (GR), plant height and soil microbial counts (Colony Forming Unit, CFU) of maize 66 days after sowing (2006)

Treatment	Biomass (g pot^{-1})			GR (%)	Plant height (cm)	Soil microbial counts (CFU)		
	Roots	Shoots	Total			Bacteria	Actino-mycetes	Fungi
Control	10.10	------*	----*	100	81.0	5220178	1912342	2480877
Control	11.45	------*	----*	100	78.3	5157298	722021	3610108
Control	12.77	------*	----*	100	81.7	6811146	1212590	2063983
Control	11.33	16.03	27.36	100	72.3	5092496	597588	2909998
Control	8.38	16.95	25.33	100	66.3	5400991	395194	3187902
Control	6.56	------*	----*	100	60.3	------*	------*	------*
La1	9.49	------*	----*	100	83.3	35101404	2366095	2626105
La1	6.89	17.66	24.55	100	84.3	14991729	439412	2481390
La1	10.79	------*	----*	100	83.3	------*	------*	-------*
La1	7.06	------*	----*	100	70.3	20083464	938967	1825769
La1	12.94	------*	----*	100	70.7	43076923	1641026	1871795
La1	10.54	------*	----*	100	87.3	23539044	1330468	1867772
La2	9.05	------*	----*	100	83.7	38891209	2714554	1905408
La2	8.26	16.98	25.24	100	83.3	20686802	1758378	1991105
La2	12.61	17.82	30.43	100	76.3	27613009	1789732	1252812
La2	6.52	15.89	22.41	100	73.0	29635021	2547572	2053655
La2	8.52	20.44	28.96	100	87.7	30662093	1637044	2884316
La2	9.01	------*	----*	100	76.3	22777254	1989737	2251545
La3	9.22	------*	----*	100	86.7	52506596	3693931	2717678
La3	10.08	------*	----*	100	83.3	46310915	1973476	1473529
La3	10.61	------*	----*	100	81.7	35225968	2009185	1722158
La3	9.42	------*	----*	100	83.7	43699927	1820830	2627198
La3	5.99	------*	----*	100	73.0	30867400	3112679	2230753
La3	8.93	------*	----*	100	803	34018905	2103459	2415083
La4	----*	------*	----*	0.00	42.6	52060855	2104014	1861243
La4	9.36	------*	----*	100	81.7	47367319	1936564	2067413
La4	12.87	22.21	35.08	100	81.7	37313433	1839760	1736111
La4	11.34	21.40	32.74	100	83.0	43166597	1569694	1360402
La4	11.05	25.19	36.24	100	88.3	25139954	1192204	2047481
La4	13.43	24.56	37.99	100	84.7	37560875	984354	1813284
Ce1	12.00	24.42	36.42	100	80.0	24721557	2107838	1925679
Ce1	9.59	20.95	30.54	100	78.7	13865634	1177271	1935956
Ce1	13.64	25.94	39.58	100	83.0	55723362	2473701	1562337
Ce1	10.19	------*	----*	100	84.0	42926367	1975140	1790793
Ce1	9.99	22.53	32.52	100	79.7	33923460	2226227	3233330
Ce1	12.85	25.31	38.16	100	82.0	2098856	3148284	2597334
Ce2	12.05	24.80	36.85	100	84.7	20152956	516742.5	2402852
Ce2	11.06	24.23	35.29	100	89.7	32333161	1655458	1836524
Ce2	11.65	26.36	38.01	100	82.0	41059808	774713	1859312
Ce2	8.62	------*	----*	100	79.0	32237607	2351760	3329458
Ce2	10.12	23.36	33.48	100	77.7	33168369	1210909	2527114
Ce2	12.62	25.58	38.20	100	79.3	31233732	1691827	2056221
Ce3	13.01	22.61	35.62	100	82.3	54511473	2154501	1687260
Ce3	10.23	------*	----*	100	88.0	56897854	1429188	2049401
Ce3	15.50	24.81	40.31	100	84.0	35751295	1994819	1398964
Ce3	10.33	24.13	34.46	100	81.7	30991736	1368802	1859504
Ce3	11.11	27.04	38.15	100	83.7	43507712	1667361	2813672
Ce3	11.09	24.86	35.95	100	79.3	38282818	2032950	3009822
Ce4	12.93	22.82	35.75	100	75.3	31811968	1104217	1419708
Ce4	12.75	26.39	39.14	100	87.0	22860372	1232919	1515463
Ce4	14.98	26.26	41.24	100	82.0	31759967	774633	2143152
Ce4	8.99	20.23	29.22	100	79.3	38580247	1676245	2155172
Ce4	10.24	22.27	32.51	100	78.3	29039618	1063057	1659407
Ce4	12.32	23.5	35.82	100	75.3	29015544	621761	2979275
Ca1	13.95	27.33	41.28	100	82.7	17622059	1166166	1788121
Ca1	12.75	25.87	38.62	100	86.7	62060405	1706661	1629086
Ca1	12.42	26.15	38.57	100	86.7	65185649	1381936	1851272
Ca1	4.59	12.89	17.48	100	59.3	21565667	781755	2884408
Ca1	12.47	24.85	37.32	100	82.3	38234990	1162550	1679239

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Ca1	8.65	24.75	33.40	100	71.3	30224075	781657	2683689
Ca2	11.54	24.16	35.70	100	83.0	46803889	1422218	1137774
Ca2	8.81	20.62	29.43	100	74.7	36642412	1247401	2598753
Ca2	11.88	23.35	35.23	100	80.0	37290242	1916304	1165320
Ca2	8.23	------*	----*	100	75.3	35733333	1973333	2320000
Ca2	12.30	26.62	38.92	100	82.7	43076764	1315518	1779818
Ca2	9.56	20.89	30.45	100	65.3	31469632	1153886	2596245
Ca3	8.02	------*	----*	100	76.3	40476190	687830	2486772
Ca3	7.09	21.66	28.75	100	76.3	50960824	26011254	2229536
Ca3	14.47	24.62	39.09	100	85.3	60994683	6255865	2007090
Ca3	12.37	22.28	34.65	100	81.7	35844156	8051948	1662338
Ca3	9.01	20.94	29.95	100	81.7	41205925	5998331	2660129
Ca3	10.29	24.19	34.48	100	71.3	42818115	6041820	2311653
Ca4	12.54	21.98	34.52	100	82.0	58725704	12472716	2442574
Ca4	10.57	20.04	30.61	100	75.7	42721519	2452532	1845992
Ca4	9.73	21.17	30.90	100	70.7	33308854	5507763	2439152
Ca4	8.50	------*	----*	100	72.7	36409057	6112469	2258956
Ca4	9.41	21.63	31.04	100	76.0	45873992	9546033	3261561
Ca4	5.23	13.69	18.92	66.7	59.3	38719244	247144	2553822
REE1	9.71	21.61	31.32	100	77.3	32294833	3745115	2306774
REE1	11.22	21.91	33.13	100	80.3	41158863	3207184	1817404
REE1	12.21	24.2	36.41	100	77.7	41688516	2674358	2726796
REE1	9.29	17.53	26.82	100	80.3	31161621	2461506	1649733
REE1	7.33	18.66	25.99	100	71.0	47515396	2601402	4645360
REE1	11.07	24.21	35.28	100	80.0	36392405	2558017	3691983
REE2	8.53	16.92	25.45	100	79.3	28985507	2388621	1798175
REE2	8.86	23.33	32.19	100	76.3	31725888	2035745	4177242
REE2	9.11	21.68	30.79	100	82.0	26152861	2962212	3442570
REE2	8.85	24.17	33.02	100	76.7	23738398	11202390	4160888
REE2	8.67	23.17	31.84	100	80.0	39775761	9877202	3950881
REE2	8.98	23.96	32.94	100	74.7	33294268	11453228	4075218
REE3	6.30	15.25	21.55	100	71.7	41408421	2537935	3873691
REE3	6.27	19.02	25.29	100	70.0	33573270	2551569	2632144
REE3	11.34	26.71	38.05	100	76.0	35710535	3124672	3255961
REE3	8.12	20.9	29.02	100	76.7	35293493	9022397	4113151
REE3	9.72	24.33	34.05	100	80.3	46320665	2131803	3921465
REE3	5.50	14.63	20.13	100	57.7	36906290	802310	4653402
REE4	7.43	18.89	26.32	66.7	61.7	33844527	3225806	3490217
REE4	3.10	8.42	11.52	66.7	49.0	34809780	3563206	2494244
REE4	5.18	10.77	15.95	100	56.0	37016575	2707182	2513812
REE4	1.95	3.98	5.93	66.7	49.7	31172770	3089193	1853516
REE4	2.85	8.36	11.21	100	51.3	43878894	2358491	4031373
REE4	3.49	9.65	13.14	100	46.3	33037262	3330806	2247617

* no data

Appendix

Table C.2 (b): Analytical data of biomass production, germination rate (GR), plant height and soil microbial counts (Colony Forming Unit, CFU) of oilseed rape 66 days after sowing (2006)

Treatment	Biomass (g pot^{-1})			GR (%)	Plant height (cm)	Soil microbial counts (CFU)		
	Roots	Shoots	Total			Bacteria	Actino-mycetes	Fungi
Control	5.65	6.64	12.29	100	41.3	4885993	1970159	3178523
Control	3.31	-----*	-----*	100	27.8	5208333	2067630	3847362
Control	4.51	10.34	14.85	100	27.3	4499379	1577369	3232313
Control	4.69	9.14	13.83	75.0	26.3	4837338	12492026	3588135
Control	4.43	8.54	12.97	100	33.0	5158399	2240517	3230513
Control	4.12	10.41	14.53	100	23.0	5003611	464252	3688229
La1	3.80	10.76	14.56	100	33.3	41480867	2644405	518510
La1	3.45	9.17	12.62	100	28.5	30777985	1293193	15259673
La1	5.84	10.53	16.37	100	27.3	52066981	1255887	12297227
La1	4.99	7.37	12.36	75.0	27.8	34517821	1685754	8830140
La1	3.66	8.81	12.47	100	31.0	30334728	1542887	6276151
La1	3.92	8.78	12.70	100	25.8	3764509	2561958	9672697
La2	4.79	-----*	-----*	100	35.0	18808777	2272727	4127482
La2	4.97	6.81	11.78	100	40.0	21999576	1987913	3816794
La2	2.84	----*	----*	100	32.8	18376478	1278364	4048152
La2	3.70	-----*	-----	100	25.5	17465862	2275855	15348788
La2	4.45	10.25	14.70	100	22.3	18022657	1467559	3861998
La2	3.21	9.22	12.43	100	23.0	21063033	3536509	4030580
La3	3.45	------*	----*	75.0	36.3	18370607	2422790	4020234
La3	3.32	-------*	----*	100	29.3	22690870	2562734	4111052
La3	3.83	------*	-----*	100	25.0	17464289	10322177	4014180
La3	4.24	8.30	12.54	100	28.3	21425585	1959657	3762542
La3	4.19	7.61	11.80	100	32.3	15441631	3705991	3628783
La3	3.81	9.51	13.32	100	22.5	19318302	2672806	4207685
La4	4.11	-----*	-----*	75.0	25.0	20624478	1592523	3628864
La4	3.64	------*	-----*	100	34.8	13846797	1698192	4023409
La4	3.79	7.15	10.94	100	24.5	16645529	23250898	4227436
La4	5.39	9.16	14.55	100	21.8	20706647	1782344	12581254
La4	4.95	10.11	15.06	100	28.8	13969371	2302359	4009727
La4	5.08	------*	-----*	100	31.0	3481380	2611035	3270387
Ce1	4.24	------*	----*	100	33.3	3442029	2173913	3157350
Ce1	4.49	------*	----*	100	28.0	3070678	910794	3955449
Ce1	4.66	9.89	14.55	100	42.0	3467153	2241919	3415016
Ce1	3.62	9.21	12.83	100	31.0	3613946	2497874	3348214
Ce1	3.80	8.56	12.36	100	27.3	3511236	2861007	3485227
Ce1	1.66	7.17	8.83	75.0	28.8	3471836	2333074	1249861
Ce2	3.93	9.03	12.96	100	27.5	3294178	1251277	3013279
Ce2	4.51	10.00	14.51	100	32.5	3006646	1529697	3982488
Ce2	3.45	9.37	12.82	100	35.5	3172720	2450475	13413124
Ce2	5.27	11.03	16.30	100	33.0	3245742	1246365	11165351
Ce2	3.79	10.36	14.15	100	33.0	4731284	1202426	3319741
Ce2	4.23	9.07	13.30	100	30.0	3804290	1611540	3381591
Ce3	3.61	9.16	12.77	100	30.5	4194631	2805159	3591653
Ce3	2.11	7.94	10.05	100	39.0	3916930	4994742	2970557
Ce3	5.12	9.00	14.12	100	36.0	2933306	1981268	3859613
Ce3	3.89	9.00	12.89	100	33.3	3711723	1108362	10568100
Ce3	4.65	10.15	14.8	100	23.0	3851091	2353445	3851091
Ce3	3.53	8.89	12.42	100	24.8	3573632	102838	3290827
Ce4	3.09	8.29	11.38	100	32.8	3896724	2915916	10603329
Ce4	4.61	8.86	13.47	100	26.0	4006326	2398524	8697944
Ce4	4.03	9.82	13.85	100	40.3	2905469	985784	9857840
Ce4	4.95	9.78	14.73	100	26.0	3709810	2061006	4070486
Ce4	2.37	9.23	11.6	100	26.8	4171387	2291688	18024513
Ce4	3.00	8.27	11.27	100	24.0	3628783	1080914	13125386
Ca1	4.62	9.29	13.91	100	32.0	3693300	2340824	12744486
Ca1	6.13	11.49	17.62	100	36.8	3654143	1801338	12352033
Ca1	4.14	9.61	13.75	100	27.0	3648113	2188868	3569940
Ca1	3.47	8.10	11.57	100	22.3	3560955	3220570	2827817
Ca1	5.63	9.25	14.88	100	31.3	4130525	1419868	13940520

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Ca1	4.51	9.75	14.26	100	28.5	3812807	2533166	3838922
Ca2	4.41	11.18	15.59	100	35.5	3604125	2920130	3393665
Ca2	5.63	8.87	14.5	100	25.3	3859983	2194374	4177242
Ca2	3.33	8.74	12.07	100	29.5	3388947	1772680	3023983
Ca2	4.75	8.77	13.52	100	24.8	3464931	2467451	13124738
Ca2	4.34	9.90	14.24	100	32.3	3913226	2836432	8404244
Ca2	4.20	11.62	15.82	100	39.3	3165225	1793627	11605824
Ca3	5.05	9.23	14.28	100	33.3	3782740	2608786	3234895
Ca3	5.28	9.31	14.59	100	34.0	3496322	3081943	2978349
Ca3	4.37	9.72	14.09	100	29.5	3278859	2914541	3539086
Ca3	4.88	10.01	14.89	100	31.0	3873349	3613393	4055319
Ca3	3.77	10.97	14.74	100	36.3	4133306	2651555	3145472
Ca3	4.13	9.37	13.5	100	44.0	3768055	3401717	3637220
Ca4	3.62	7.48	11.1	100	24.8	4573996	8660821	2598246
Ca4	3.43	10.42	13.85	100	33.0	1542564	7843547	3895629
Ca4	2.60	8.32	10.92	100	31.3	4002534	2361207	1468556
Ca4	4.11	11.21	15.32	100	28.8	3997896	2288269	3577065
Ca4	2.76	10.86	13.62	100	31.3	4906054	2505219	16440501
Ca4	4.56	11.31	15.87	100	38.5	4834854	1358105	4128640
REE1	4.09	10.63	14.72	100	39.0	4142888	2688762	4197761
REE1	5.19	9.56	14.75	75.0	33.3	3742515	2064836	2529424
REE1	3.69	9.70	13.39	100	35.8	3597697	18681377	10393348
REE1	3.02	9.10	12.12	100	28.3	3409333	9615385	415512
REE1	3.66	9.77	13.43	100	33.5	4500906	1491424	4287845
REE1	4.36	10.45	14.81	100	31.5	3641413	1126480	4505921
REE2	1.97	7.48	9.45	100	26.5	3013012	1386519	2666382
REE2	2.27	9.57	11.84	100	33.5	3191950	1379572	3164899
REE2	5.92	10.8	16.72	100	25.3	4273280	3434354	3565436
REE2	3.87	10.86	14.73	100	13.3	3533100	2390819	11157157
REE2	3.52	9.18	12.7	75.0	21.0	4197466	1135164	3986272
REE2	4.63	11.02	15.65	100	30.7	3763846	2796000	4032692
REE3	4.54	9.55	14.09	100	24.8	4109662	2041574	10340439
REE3	4.32	8.23	12.55	100	26.5	3844930	1034154	10606703
REE3	4.71	10.04	14.75	100	28.8	3255069	1814301	3415155
REE3	2.91	9.96	12.87	100	25.8	4133333	2986667	12266667
REE3	3.27	5.64	8.91	100	27.8	3779191	1407423	13292327
REE3	3.76	11.27	15.03	100	26.8	3487767	1301406	3409682
REE4	5.31	9.21	14.52	100	20.8	3642940	2463571	2804277
REE4	3.37	7.69	11.06	100	20.3	3628178	1615466	1191737
REE4	2.64	10.86	13.5	100	25.3	2997914	1590198	3180396
REE4	1.94	8.18	10.12	100	16.0	2275819	1177148	2380454
REE4	2.58	8.29	10.87	100	21.5	3294634	2405606	3163895
REE4	2.77	12.18	14.95	100	29.0	3539117	3166578	3459287

* no data

Appendix

Table C.3: Analytical data of soil pH, soil conductivity (EC) and some soil enzyme activities (AlP, alkaline phosphatase activity and DHA, dehydrogenase activity) of maize, oilseed rape and non-vegetated soil after 66 days of sowing (2005)

Treatment	Maize				Oilseed rape				Non-vegetated soil			
	Soil pH (1:2.5)	EC (mS m^{-1})	AlP (µg p-NP g^{-1})	DHA (µg TPF g^{-1} dm d^{-1})	Soil pH (1:2.5)	EC (mS m^{-1})	AlP (µg p-NP g^{-1})	DHA (µg TPF g^{-1} dm d^{-1})	Soil pH (1:2.5)	EC (mS m^{-1})	AlP (µg p-NP g^{-1})	DHA (µg TPF g^{-1} dm d^{-1})
Control	5.35	134	61.2	16.4	5.56	140	130.0	21.2	6.20	455	177.7	3.9
Control	4.85	85	53.9	18.8	5.10	135	132.1	18.6	6.34	368	190.9	2.0
Control	5.18	141	73.1	14.0	5.49	193	167.8	15.9	6.25	438	185.1	3.0
Control	5.19	160	100.8	17.3	5.47	148	105.4	22.4	6.07	348	187.6	3.1
La1	5.39	105	86.2	15.8	5.63	83	63.8	22.0	6.28	429	220.5	3.3
La1	5.04	104	68.5	21.5	5.00	94	74.0	17.9	6.31	357	214.2	2.5
La1	5.28	167	85.1	18.8	5.07	126	66.4	18.1	6.04	374	160.7	3.0
La1	5.38	143	84.9	17.0	5.40	146	5.5	18.6	6.16	386	163.9	3.4
La2	5.40	138	125.8	17.0	5.46	127	86.0	22.0	6.16	430	213.6	4.1
La2	5.24	149	60.7	14.4	5.44	161	105.5	16.5	6.14	425	199.6	5.6
La2	5.24	179	56.4	13.1	5.29	145	105.1	18.5	6.16	409	194.9	2.1
La2	5.35	137	269.7	16.6	5.44	120	108.0	21.0	6.20	376	210.6	4.3
La3	5.45	111	123.0	19.8	5.47	134	117.2	21.5	6.16	465	209.7	3.6
La3	5.30	113	106.3	17.3	5.67	150	144.9	22.7	5.98	370	210.8	3.2
La3	5.31	102	82.7	20.8	5.62	166	127.1	23.4	6.09	421	222.5	5.2
La3	5.04	126	88.2	18.1	5.36	121	75.8	19.5	5.98	401	200.6	4.1
La4	5.38	124	147.6	21.5	5.60	155	83.6	21.3	5.99	402	204.7	2.0
La4	5.34	164	79.4	11.4	5.20	114	96.5	19.5	5.92	379	192.6	3.3
La4	5.09	104	122.9	19.0	5.09	138	83.4	19.0	5.85	407	168.7	2.6
La4	5.36	143	133.0	19.0	5.56	156	102.8	16.7	5.99	426	224.5	2.8
Ce1	5.59	114	134.0	20.9	5.65	97	131.7	22.6	6.01	389	188.3	4.2
Ce1	5.36	226	120.3	13.6	5.14	134	69.6	20.7	5.92	397	129.5	3.8
Ce1	5.42	114	74.6	15.2	5.26	149	92.7	18.4	6.04	376	121.9	2.2
Ce1	5.50	142	95.1	17.3	5.08	117	74.8	18.6	6.24	418	169.9	2.6
Ce2	5.42	181	110.9	12.0	5.56	149	160.1	17.7	6.07	379	173.6	3.2
Ce2	5.33	116	109.9	15.4	5.01	133	103.1	17.2	5.99	375	158.8	3.2
Ce2	5.49	245	55.3	10.5	5.02	104	132.9	17.4	5.97	376	120.4	2.2
Ce2	5.38	140	114.9	15.3	5.26	127	113.1	19.4	5.91	396	113.4	4.8
Ce3	5.45	193	130.8	12.5	5.48	128	152.5	21.4	5.92	356	182.2	3.3
Ce3	5.36	69	92.2	20.4	5.27	119	85.4	20.2	6.09	400	212.8	3.0
Ce3	5.27	109	118.3	14.3	5.18	121	75.8	19.4	6.00	368	186.9	2.8
Ce3	5.31	94	86.2	14.9	5.53	100	109.1	23.0	5.94	402	188.5	2.5
Ce4	5.51	113	67.9	15.8	5.65	122	122.8	21.8	6.21	390	233.4	3.2
Ce4	5.1	102	65.3	15.2	5.54	130	89.8	24.9	6.31	367	205.9	2.1
Ce4	5.29	95	47.6	15.2	5.50	125	115.1	24.4	6.07	398	174.7	1.7

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Ce4	5.36	176	102.9	15.1	5.52	137	107.8	21.9	6.01	445	191.0	5.0	
Ca1	5.36	173	96.8	11.1	5.62	126	82.5	26.3	6.21	395	67.3	3.5	
Ca1	5.12	110	72.3	15.8	5.55	122	107.3	26.7	6.16	383	177.4	2.8	
Ca1	5.27	178	42.8	11.1	5.52	116	90.7	24.5	6.20	373	163.1	1.9	
Ca1	5.38	147	82.1	13.9	5.52	137	115.4	21.5	6.16	408	62.2	3.0	
Ca2	5.46	232	61.7	8.7	5.53	131	85.2	21.0	6.18	378	118.8	4.5	
Ca2	5.43	206	131.8	16.0	5.58	163	91.3	21.5	6.20	397	106.5	3.4	
Ca2	5.32	138	106.3	17.3	5.63	133	97.6	23.6	6.14	369	324.8	4.0	
Ca2	5.49	190	83.8	15.5	5.65	176	81.4	16.1	6.08	402	77.2	3.2	
Ca3	5.51	289	52.7	9.0	5.86	267	122.0	15.9	6.18	415	89.5	2.1	
Ca3	5.7	354	55.6	11.9	5.67	240	109.9	16.7	6.28	427	127.4	2.1	
Ca3	5.61	257	69.0	9.2	5.54	276	38.6	13.2	6.21	435	134.0	2.2	
Ca3	5.63	341	111.5	7.9	5.36	325	291.5	8.2	6.22	432	398.9	3.4	
Ca4	5.85	327	152.3	11.6	5.56	424	73.5	9.0	6.18	502	119.0	4.6	
Ca4	6.05	418	128.4	9.3	5.94	402	93.1	13.4	6.14	474	154.5	3.5	
Ca4	6.05	382	195.9	15.6	5.86	403	66.7	12.1	6.19	512	104.5	3.5	
Ca4	6.02	336	219.9	16.9	5.71	377	56.8	11.2	6.14	496	101.9	5.5	
REE1	5.47	152	64.9	17.0	5.67	129	103.5	24.8	5.93	423	127.0	4.5	
REE1	5.31	98	68.1	19.6	5.31	140	78.7	18.4	5.88	371	144.0	3.8	
REE1	5.34	137	78.1	14.8	5.30	158	84.6	21.0	5.87	404	104.4	3.8	
REE1	5.34	103	39.3	20.6	5.46	124	102.7	23.3	6.16	432	170.6	1.6	
REE2	5.82	130	89.8	13.8	5.59	125	96.3	25.2	6.11	373	86.2	4.0	
REE2	5.43	155	48.0	13.4	5.65	147	84.9	19.1	6.12	360	148.3	4.7	
REE2	5.53	176	72.7	13.7	5.43	146	101.4	19.1	6.15	388	179.9	3.4	
REE2	5.4	182	70.6	13.9	5.46	136	117.0	20.7	6.04	459	91.1	3.2	
REE3	5.53	162	66.1	12.0	5.44	139	102.9	22.2	6.14	365	167.8	2.7	
REE3	5.31	139	59.8	12.8	5.69	125	135.3	20.0	6.10	368	190.5	3.7	
REE3	5.32	139	40.0	12.5	5.43	148	145.7	22.0	6.11	394	182.0	2.6	
REE3	5.35	179	54.7	14.1	5.53	155	138.7	24.0	6.12	393	195.6	2.7	
REE4	5.59	206	60.5	10.9	5.28	292	51.9	6.6	6.01	426	74.3	2.5	
REE4	5.64	176	61.6	12.5	5.70	125	99.4	18.9	6.01	379	175.8	2.8	
REE4	5.51	149	60.0	12.7	5.42	201	106.8	11.9	5.95	362	180.3	2.4	
REE4	5.53	123	73.8	13.4	5.68	163	86.8	19.6	6.06	452	97.5	1.0	
Cu1	5.60	247	70.9	7.8	5.67	112	320.1	17.8	6.15	384	206.5	3.3	
Cu1	5.37	118	127.8	18.1	5.75	208	186.1	16.8	6.20	377	151.4	3.6	
Cu1	5.27	102	96.8	13.7	5.63	150	125.2	20.6	6.04	363	124.0	3.8	
Cu1	5.46	85	122.2	17.4	5.55	129	82.1	17.5	6.11	398	127.7	4.7	
Cu2	5.41	59	58.3	14.1	6.05	125	45.7	12.1	6.20	388	117.5	3.3	
Cu2	5.48	104.9	78.7	8.6	5.41	198	60.3	4.7	6.14	337	121.2	0.2	
Cu2	5.23	97	43.4	13.7	5.61	176	97.0	9.9	5.96	361	70.1	2.2	
Cu2	5.57	198	42.1	8.6	5.65	188	42.7	12.0	6.14	427	74.1	4.7	

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Cu3	5.63	210	54.6	2.7	5.83	231	53.9	3.2	5.97	361	58.5	1.8
Cu3	5.46	292	25.7	0.9	5.42	244	43.4	1.3	5.97	399	74.5	0.2
Cu3	5.58	254	62.0	3.1	5.39	218	47.1	0.9	5.97	399	78.4	0.5
Cu3	5.71	187	35.9	2.1	5.59	243	164.1	0.8	6.01	416	74.7	0.6
Cu4	5.03	324	0.8	1.4	5.28	253	128.8	0.3	5.76	353	13.9	0.1
Cu4	5.63	250	54.4	1.6	5.46	212	116.4	0.7	5.85	372	27.2	-0.3
Cu4	5.66	251	52.2	-0.5	5.35	204	110.0	0.6	5.80	377	25.0	0.9
Cu4	5.82	231	36.0	1.4	5.21	186	142.0	-0.7	5.77	390	37.1	0.4

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Table C.4: Analytical data of rare earth elements content (µg g^{-1}) of maize and oilseed rape after 66 days of sowing (2005)

Treatment	Maize								Oilseed rape							
	Roots				Shoots				Roots				Shoots			
	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd
Control	2.8	5.7	0.64	2.25	0.05	0.06	<LQ	0.02	1.4	2.6	0.26	0.89	0.05	0.06	<LQ	0.02
Control	1.8	3.4	0.36	1.29	0.03	0.04	<LQ	0.02	1.9	3.8	0.36	1.26	0.07	0.08	<LQ	0.03
Control	1.7	3.5	0.36	1.26	0.03	0.04	<LQ	0.02	1.7	3.2	0.32	1.11	0.05	0.07	<LQ	0.04
Control	1.5	3.0	0.33	1.14	0.03	0.04	<LQ	0.02	1.5	2.9	0.29	1.01	0.06	0.06	<LQ	0.03
La1	2.3	4.0	0.42	1.49	0.04	0.04	<LQ	<LQ	2.5	4.5	0.44	1.55	0.06	0.06	<LQ	0.03
La1	1.6	2.6	0.27	0.94	0.05	0.04	<LQ	<LQ	1.5	2.3	0.23	0.82	0.06	0.06	<LQ	0.03
La1	1.6	2.7	0.29	0.99	0.04	0.05	<LQ	<LQ	2.2	3.2	0.31	1.08	0.07	0.06	<LQ	0.04
La1	2.3	3.8	0.40	1.42	0.03	0.04	<LQ	<LQ	2.2	3.2	0.31	1.07	0.08	0.07	<LQ	0.03
La2	4.0	3.9	0.41	1.44	0.06	0.03	<LQ	<LQ	6.0	2.5	0.24	0.84	0.16	0.06	<LQ	0.03
La2	4.8	3.9	0.41	1.47	0.07	0.03	<LQ	<LQ	3.3	2.0	0.20	0.68	0.13	0.07	<LQ	0.03
La2	4.4	4.2	0.45	1.62	0.06	0.03	<LQ	<LQ	5.1	2.4	0.23	0.79	0.16	0.08	<LQ	0.04
La2	4.0	4.1	0.43	1.55	0.09	0.04	<LQ	<LQ	5.4	4.6	0.46	1.61	0.18	0.10	<LQ	0.03
La3	11.1	3.2	0.32	1.12	0.23	0.04	<LQ	<LQ	11.9	2.7	0.26	0.92	0.44	0.07	<LQ	0.03
La3	7.4	3.2	0.33	1.16	0.16	0.04	<LQ	<LQ	21.9	2.4	0.22	0.77	0.70	0.07	<LQ	0.03
La3	12.9	3.2	0.33	1.16	0.36	0.04	<LQ	<LQ	16.7	3.4	0.33	1.17	1.20	0.09	<LQ	0.04
La3	9.2	3.9	0.42	1.46	0.19	0.04	<LQ	<LQ					0.77	0.09	<LQ	0.04
La4	30.1	2.9	0.29	0.98	0.61	0.05	<LQ	<LQ	49.5	2.5	0.23	0.81	2.60	0.07	<LQ	0.03
La4	25.3	3.2	0.30	1.02	0.62	0.03	<LQ	<LQ	54.8	5.3	0.51	1.78	1.19	0.09	<LQ	0.04
La4	29.5	4.4	0.45	1.53	0.71	0.06	<LQ	<LQ	66.5	4.5	0.43	1.51	1.83	0.07	<LQ	0.03
La4	33.7	3.3	0.34	1.16	0.80	0.03	<LQ	<LQ	47.5	2.6	0.26	0.91	0.73	0.07	<LQ	0.03
Ce1	2.1	3.7	0.37	1.29	0.04	0.04	<LQ	<LQ	3.7	3.6	0.35	1.23	0.08	0.07	<LQ	0.03
Ce1	2.6	5.8	0.56	1.94	0.03	0.04	<LQ	<LQ	2.5	4.3	0.39	1.34	0.09	0.10	<LQ	0.04
Ce1	1.8	3.9	0.37	1.27	0.04	0.05	<LQ	<LQ	1.4	2.7	0.24	0.80	0.09	0.14	<LQ	0.05
Ce1	1.5	2.9	0.28	0.96	0.04	0.05	<LQ	<LQ	2.4	4.4	0.42	1.45	0.07	0.08	<LQ	0.03
Ce2	1.5	4.4	0.31	1.06	0.03	0.07	<LQ	0.02	1.8	4.7	0.33	1.17	0.05	0.08	<LQ	
Ce2	1.6	4.4	0.33	1.15	0.03	0.06	<LQ	<LQ	2.1	5.9	0.38	1.31	0.06	0.14	<LQ	0.03
Ce2	7.4	21.6	1.48	5.24	0.04	0.07	<LQ	<LQ	2.3	6.6	0.44	1.55	0.06	0.11	<LQ	0.03
Ce2	1.9	6.1	0.39	1.37			<LQ	<LQ	1.8	5.2	0.35	1.22	0.07	0.15	<LQ	0.04
Ce3	2.8	11.1	0.58	2.04	0.02	0.06	<LQ	<LQ	1.4	8.1	0.25	0.90	0.07	0.30	<LQ	0.04
Ce3	2.1	10.5	0.44	1.54	0.04	0.22	<LQ	<LQ	1.6	11.9	0.29	1.04	0.09	0.44	<LQ	0.04
Ce3	2.7	12.8	0.56	1.94	0.04	0.19	<LQ	<LQ	1.9	10.5	0.36	1.29	0.06	0.36	<LQ	0.03
Ce3	2.4	11.6	0.52	1.81	0.03	0.13	<LQ	<LQ	1.4	8.9	0.27	0.96	0.05	0.22	<LQ	0.03
Ce4	2.9	28.7	0.62	2.13	0.03	0.54	<LQ	<LQ	2.8	46.6	0.50	1.79	0.07	0.77	<LQ	0.03
Ce4	3.2	41.3	0.67	2.32	0.03	0.31	<LQ	<LQ	1.5	30.5	0.28	0.97	0.06	1.07	<LQ	0.02
Ce4	2.6	32.1	0.54	1.88	0.03	0.37	<LQ	<LQ	2.1	21.6	0.39	1.38	0.06	0.73	<LQ	0.03
Ce4	2.1	26.5	0.43	1.50	0.02	0.20	<LQ	<LQ	1.6	56.1	0.29	1.03	0.09	1.88	<LQ	0.03
Ca1	3.0	6.9	0.62	2.17	0.02	0.04	<LQ	<LQ	1.3	2.8	0.25	0.86	0.07	0.16	<LQ	0.04

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Ca1	2.0	4.4	0.44	1.53	0.02	0.03	<LQ	<LQ	2.4	4.6	0.45	1.58	0.08	0.12	<LQ	0.04
Ca1	2.0	4.1	0.42	1.46	0.04	0.06	<LQ	<LQ	1.9	3.7	0.35	1.22	0.05	0.09	<LQ	0.03
Ca1	2.8	5.6	0.59	2.07			<LQ	0.02	1.7	3.3	0.31	1.08	0.06	0.10	<LQ	0.03
Ca2	2.3	4.8	0.50	1.77	0.02	0.06	<LQ	<LQ	1.3	2.5	0.24	0.83	0.06	0.10	<LQ	0.03
Ca2	1.7	3.5	0.36	1.25	0.02	0.04	<LQ	<LQ	1.4	2.5	0.24	0.80	0.06	0.09	<LQ	0.03
Ca2					0.55	0.87	<LQ	<LQ	1.6	2.9	0.28	0.99	0.05	0.07	<LQ	
Ca2							<LQ	0.11	1.7	3.1	0.30	1.06	0.06	0.10	<LQ	0.03
Ca3							<LQ	<LQ	1.4	2.7	0.28	0.97	0.11	0.19	<LQ	0.06
Ca3							<LQ	<LQ	1.5	2.8	0.28	1.00	0.06	0.08	<LQ	0.03
Ca3							<LQ	<LQ					0.04	0.07	<LQ	
Ca3							<LQ	<LQ							<LQ	
Ca4							<LQ	<LQ							<LQ	
Ca4							<LQ	<LQ							<LQ	
Ca4							<LQ	<LQ							<LQ	
Ca4							<LQ	<LQ							<LQ	
REE1	3.8	7.7	0.80	2.84	0.04	0.05	<LQ	0.02	3.2	6.0	0.60	2.10	0.09	0.14	<LQ	0.04
REE1	4.2	8.3	0.86	3.04	0.05	0.06	<LQ	0.03	3.0	5.2	0.51	1.71	0.09	0.13	<LQ	0.04
REE1	4.9	9.8	1.01	3.62	0.04	0.06	<LQ	0.02	2.6	4.9	0.49	1.69	0.06	0.08	<LQ	0.02
REE1	3.7	7.5	0.77	2.71	0.05	0.06	<LQ	<LQ	2.6	4.8	0.46	1.56	0.06	0.08	<LQ	0.02
REE2	7.0	12.9	1.34	4.55	0.10	0.11	<LQ	0.04	3.8	6.8	0.68	2.29	0.12	0.14	<LQ	0.04
REE2	6.0	11.2	1.14	3.87	0.08	0.09	<LQ	0.03	5.0	8.1	0.80	2.54	0.21	0.24	0.025	0.07
REE2	6.9	12.8	1.32	4.58	0.08	0.11	<LQ	0.03	3.9	6.6	0.65	2.16	0.21	0.24	0.025	0.07
REE2	11.7	21.7	2.26	7.44	0.11	0.12	<LQ	0.04	6.1	10.4	1.02	3.35	0.18	0.21	<LQ	0.06
REE3	26.1	42.3	4.36	14.21	0.74	0.86	0.09	0.27	10.5	16.6	1.67	5.48	0.23	0.25	0.027	0.08
REE3	18.5	31.8	3.31	10.56	0.28	0.31	0.03	0.10	17.4	26.9	2.69	8.61	0.67	0.81	0.082	0.25
REE3	20.0	33.5	3.37	10.75	0.19	0.20	<LQ	0.07	23.0	34.4	3.41	10.90	0.80	0.82	0.079	0.25
REE3	38.4	59.0	5.92	19.21	0.45	0.45	0.05	0.16	28.9	43.1	4.31	14.06	0.74	0.82	0.081	0.26
REE4	34.8	55.4	5.54	17.88	0.58	0.54	0.05	0.17	164.4	201.6	18.92	59.73	2.10	1.93	0.19	0.66
REE4	56.5	81.6	8.05	25.76	1.02	1.01	0.09	0.32	44.9	64.5	6.30	20.87	0.24	0.32	0.04	0.10
REE4	59.7	91.7	9.07	28.74	0.85	0.82	0.08	0.26	122.7	143.5	13.56	43.77	2.41	2.15	0.21	0.71
REE4							<LQ	<LQ							0.03	
Cu1	2.8	5.7	0.58	2.04	0.03	0.04	<LQ	<LQ	2.6	5.0	0.50	1.67	0.07	0.10	<LQ	0.03
Cu1	3.1	6.2	0.65	2.27	0.03	0.03	<LQ	<LQ	1.8	3.4	0.34	1.23	0.09	0.14	<LQ	0.04
Cu1	2.1	4.4	0.45	1.58	0.02	0.03	<LQ	<LQ	2.4	4.7	0.47	1.65	0.06	0.07	<LQ	0.03
Cu1	3.2	6.1	0.64	2.27			<LQ	<LQ	2.6	5.1	0.52	1.84	0.08	0.10	<LQ	0.03
Cu2	2.5	5.2	0.53	1.85	0.04	0.05	<LQ	<LQ	1.9	3.6	0.36	1.28	0.10	0.13	<LQ	0.04
Cu2	2.0	4.1	0.42	1.52	0.03	0.04	<LQ	<LQ	1.2	2.6	0.23	0.79	0.09	0.09	<LQ	0.03
Cu2	2.6	5.6	0.56	1.99	0.04	0.04	<LQ	<LQ	2.9	5.7	0.57	2.00	0.11	0.09	<LQ	0.04
Cu2					0.04	0.07	<LQ	<LQ							<LQ	0.09
Cu3					0.06	0.11	<LQ	0.05					0.44	0.23	0.03	
Cu3																

Appendix

Cu3																
Cu3																
Cu4																
Cu4																
Cu4																
Cu4																

Absent values mean no data

Appendix

Table C. 5: Rare earth elements uptake (µg pot^{-1}) by maize and oilseed rape after 66 days of sowing (2005)

Treatment	Maize								Oilseed rape							
	Uptake by roots				Uptake by shoots				Uptake by roots				Uptake by shoots			
	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd
Control	5.41	10.92	1.22	4.32	0.21	0.29		0.11	1.78	3.35	0.33	1.14	0.50	0.60		0.23
Control	14.69	28.65	2.99	10.76	0.81	1.14		0.44	3.51	6.88	0.66	2.30	0.99	1.15		0.46
Control	3.07	6.22	0.65	2.27	0.14	0.21		0.09	0.09	0.16	0.02	0.06	0.04	0.05		0.03
Control	5.14	10.21	1.09	3.84	0.26	0.38		0.18	1.36	2.63	0.26	0.91	0.62	0.68		0.32
La1	2.93	5.16	0.54	1.90	0.25	0.28			5.73	10.19	1.00	3.48	0.90	0.90		0.45
La1	9.31	14.61	1.52	5.31	1.00	0.85			4.28	6.62	0.66	2.32	1.32	1.27		0.77
La1	2.05	3.43	0.36	1.25	0.24	0.25			3.12	4.58	0.44	1.55	1.25	1.16		0.67
La1	7.22	12.01	1.26	4.46	0.33	0.38			2.43	3.57	0.34	1.19	1.00	0.88		0.39
La2	0.60	0.59	0.06	0.22	0.05	0.02			12.63	5.34	0.51	1.79	3.72	1.37		0.71
La2	8.40	6.81	0.72	2.56	0.39	0.18			1.42	0.84	0.09	0.29	0.31	0.17		0.08
La2	1.68	1.59	0.17	0.61	0.08	0.05			12.34	5.82	0.56	1.94	2.90	1.39		0.65
La2	10.27	10.63	1.12	3.99	0.83	0.37			18.70	15.83	1.58	5.54	3.32	1.82		0.63
La3	53.83	15.23	1.56	5.42	4.73	0.74			30.38	6.91	0.67	2.34	8.87	1.30		0.62
La3	11.37	4.91	0.51	1.79	0.97	0.23			41.19	4.43	0.41	1.45	11.75	1.18		0.44
La3	70.14	17.16	1.78	6.30	8.25	0.98			44.22	9.09	0.87	3.08	21.33	1.59		0.64
La3	21.75	9.20	0.98	3.45	1.78	0.37										
La4	145.2	13.81	1.38	4.75	9.71	0.78			19.32	0.97	0.09	0.32	22.89	0.64		0.28
La4	17.98	2.26	0.21	0.73	1.53	0.08			131.6	12.74	1.24	4.27	23.36	1.80		0.71
La4	212.1	32.02	3.21	11.04	19.36	1.50			61.18	4.16	0.39	1.39	28.12	1.11		0.48
La4	101.0	9.89	1.01	3.47	6.97	0.29			20.92	1.16	0.11	0.40	1.99	0.18		0.07
Ce1	9.72	17.28	1.70	5.98	0.62	0.66			11.98	11.69	1.14	3.99	1.63	1.44		0.62
Ce1	0.03	0.06	0.01	0.02	0.03	0.03			7.14	12.42	1.13	3.85	1.80	1.90		0.71
Ce1	1.57	3.31	0.32	1.09	0.21	0.28			1.10	2.12	0.18	0.63	1.19	1.75		0.58
Ce1	1.63	3.24	0.32	1.08	0.09	0.12			6.89	12.75	1.20	4.17	1.09	1.36		0.50
Ce2	0.49	1.41	0.10	0.34	0.03	0.07		0.02	0.32	0.84	0.06	0.21	0.32	0.52		
Ce2	3.41	9.48	0.71	2.52	0.23	0.52			2.10	6.02	0.39	1.34	2.50	5.50		1.34
Ce2					0.46	0.82			2.16	6.21	0.41	1.46	1.66	3.01		0.76
Ce2	7.52	23.96	1.54	5.36					5.84	16.59	1.11	3.91	4.13	8.42		2.33
Ce3	0.88	3.55	0.19	0.65	0.02	0.06			3.08	18.21	0.57	2.03	1.04	4.23		0.57
Ce3	17.70	90.62	3.80	13.25	0.97	5.56			2.43	18.57	0.45	1.62	1.08	5.09		0.51
Ce3	19.23	92.24	4.00	13.97	0.75	3.77			2.09	11.80	0.40	1.45	0.50	2.93		0.22
Ce3	3.66	17.72	0.79	2.78	0.56	2.66			2.20	13.59	0.41	1.47	1.09	4.46		0.54
Ce4	13.97	139.3	2.99	10.35	0.34	6.09			8.26	135.9	1.47	5.22	1.31	15.12		0.58
Ce4	20.86	271.5	4.38	15.25	0.61	6.79			2.33	47.60	0.43	1.52	1.00	19.45		0.46
Ce4	9.19	115.6	1.95	6.78	0.26	3.85			5.78	60.56	1.09	3.87	1.17	13.90		0.51
Ce4	2.43	31.31	0.51	1.77	0.09	0.79			1.44	49.35	0.26	0.91	1.41	30.81		0.52
Ca1	5.16	12.08	1.08	3.78	0.06	0.10		0.06	4.52	9.37	0.83	2.88	1.49	3.43		0.85

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Ca1	12.64	27.46	2.70	9.47	0.43	0.62			4.16	8.06	0.78	2.75	1.14	1.85		0.59
Ca1									7.08	14.00	1.33	4.57	1.12	1.97		0.62
Ca1									2.44	4.77	0.45	1.55	0.81	1.44		0.39
Ca2	7.64	15.84	1.64	5.81	0.18	0.52	0.54		2.01	3.74	0.35	1.25	0.72	1.23		0.36
Ca2	1.94	3.94	0.40	1.40	0.04	0.07			0.08	0.15	0.01	0.05	0.48	0.75		0.22
Ca2									2.54	4.72	0.45	1.58	0.84	1.11		
Ca2									0.95	1.76	0.17	0.61	0.27	0.47		0.14
Ca3									0.99	1.88	0.19	0.67	0.22	0.39		0.13
Ca3									0.28	0.53	0.05	0.19	0.03	0.04		0.02
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Ca4																
REE1	19.90	39.79	4.14	14.72	0.58	0.69		0.33	11.89	22.63	2.26	7.90	1.81	2.95		0.82
REE1	41.46	83.05	8.52	30.31	1.29	1.73		0.75	4.37	7.73	0.75	2.53	1.66	2.43		0.81
REE1	21.58	43.31	4.47	16.07	0.41	0.61		0.23	3.14	5.90	0.59	2.03	0.73	1.04		0.31
REE1	28.21	56.38	5.77	20.38	1.06	1.29			1.87	3.42	0.33	1.12	1.22	1.67		0.49
REE2	14.88	27.58	2.87	9.73	0.42	0.47		0.18	13.07	23.10	2.33	7.78	2.39	2.82		0.86
REE2	10.45	19.52	1.98	6.73	0.51	0.60		0.22	19.81	32.33	3.18	10.15	4.01	4.64	0.48	1.26
REE2	6.11	11.30	1.16	4.03	0.17	0.23		0.07	3.36	5.70	0.56	1.88	2.34	2.66	0.27	0.77
REE2	9.85	18.22	1.89	6.25	0.22	0.24		0.08	16.83	28.60	2.82	9.24	4.06	4.73		1.35
REE3	18.79	30.47	3.14	10.23	1.18	1.37	0.14	0.43	14.74	23.36	2.35	7.72	2.70	2.91	0.31	0.99
REE3	108.4	186.8	19.48	62.08	4.20	4.62	0.47	1.49	58.48	90.49	9.03	28.91	13.83	16.78	1.70	5.23
REE3	62.01	103.9	10.44	33.32	1.82	1.92		0.64	54.37	81.15	8.05	25.72	13.99	14.42	1.39	4.36
REE3	37.23	57.20	5.74	18.63	1.07	1.05	0.11	0.37	72.85	108.6	10.86	35.43	14.15	15.62	1.54	4.95
REE4	91.75	146.3	14.62	47.19	5.04	4.70	0.46	1.49	65.76	80.66	7.57	23.89	10.56	9.69	0.97	3.29
REE4	264.2	381.8	37.69	120.5	14.32	14.21	1.38	4.48	13.01	18.70	1.83	6.05	0.08	0.11	0.01	0.03
REE4	374.2	574.6	56.89	180.1	14.87	14.39	1.37	4.63	58.91	68.88	6.51	21.01	13.22	11.79	1.14	3.87
REE4																
Cu1	20.76	41.69	4.23	14.95	0.46	0.56			2.90	5.50	0.55	1.85	0.77	1.04		0.36
Cu1	20.06	40.55	4.23	14.82	0.40	0.49			0.96	1.85	0.18	0.66	0.26	0.42		0.13
Cu1	7.72	16.38	1.65	5.81					6.25	12.38	1.22	4.31	0.90	1.03		0.40
Cu1									1.53	2.98	0.30	1.07	0.49	0.57		0.20
Cu2	30.56	59.17	6.19	21.90	0.83	1.08			0.11	0.22	0.02	0.08	0.37	0.47		0.16
Cu2	0.20	0.42	0.04	0.15	0.01	0.01			0.31	0.65	0.06	0.20	0.19	0.18		0.07
Cu2	11.01	23.32	2.39	8.55	0.67	0.78			0.29	0.57	0.06	0.20				
Cu2	0.23	0.50	0.05	0.18	0.02	0.03										
Cu3																
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Absent values mean no data

Table C.6: Analytical data of soil pH, soil conductivity (EC) and some soil enzyme activities (AlP, alkaline phosphatase activity and DHA, dehydrogenase activity) of maize, oilseed rape and non-vegetated soil (n, 4) after 66 days of sowing (2006)

Treatment	Maize				Oilseed rape				Non-vegetated soil			
	Soil pH (1:2.5)	EC (mS m^{-1})	AlP (µg p-NP g^{-1})	DHA (µg TPF g^{-1} dm d^{-1})	Soil pH (1:2.5)	EC (mS m^{-1})	AlP (µg p-NP g^{-1})	DHA (µg TPF g^{-1} dm d^{-1})	Soil pH (1:2.5)	EC (mS m^{-1})	AlP (µg p-NP g^{-1})	DHA (µg TPF g^{-1} dm d^{-1})
Control	5.54	46.8	156.7	30.4	5.38	75.8	158.9	29.8	5.92	407	100.2	1.1
Control	5.19	44.2	89.4	18.5	5.22	65.6	146.5	27.3	6.02	385	135.2	0.0
Control	5.47	36.7	178.4	34.5	5.35	67.5	143.6	31.2	6.16	383	119.0	1.6
Control	5.10	42.1	376.1	24.5	5.06	57.7	148.3	25.4	6.05	369	151.9	0.8
Control	4.93	63.8	107.5	22.2	5.23	45.6	123.7	23.4				
Control	-----*	------*	-----*	------*	5.18	59.3	122.7	24.3				
La1	5.33	37.2	201.6	30.5	5.31	52.5	157.9	29.6	6.16	406	121.8	0.3
La1	4.92	59.5	348.3	17.3	5.29	59.1	111.1	27.0	6.33	442	106.3	1.0
La1	-------*	-------*	----*	--------*	5.25	65.4	96.2	28.0	6.20	432	121.8	1.8
La1	4.91	63.3	93.5	19.7	5.07	60.5	68.4	30.0	6.28	447	77.8	1.8
La1	5.39	17.8	141.7	24.9	5.19	33.9	106.2	29.1				
La1	5.60	17.1	123.4	28.7	5.33	59.9	123.7	28.6				
La2	5.33	32.6	442.9	28.4	5.18	34.3	120.9	21.2	5.87	355	200.6	0.6
La2	5.16	39.8	115.9	22.4	5.1	68.8	127.3	26.9	6.08	409	237.7	1.9
La2	5.48	20.7	151.0	33.5	5.1	72.9	145.5	19.8	6.09	416	171.7	0.5
La2	5.17	55.3	120.0	22.6	5.33	64.0	129.1	28.5	6.13	383	212.2	0.5
La2	5.14	38.1	134.5	21.3	5.35	53.4	117.9	26.4				
La2	5.08	40.2	125.9	22.9	5.19	68.8	155.9	24.1				
La3	5.15	36.7	191.9	31.8	5.22	53.2	126.8	26.9	6.20	360	151.0	1.9
La3	5.21	33.0	188.9	32.3	5.13	54.7	136.3	27.3	6.08	361	114.4	0.3
La3	5.29	28.3	185.2	32.2	5.13	45.0	116.7	24.4	6.16	369	157.3	0.2
La3	5.29	31.7	143.4	30.4	5.26	54.5	130.8	25.9	6.26	401	156.6	1.6
La3	5.07	68.9	159.2	20.7	5.3	71.4	140.5	28.5				
La3	5.15	44.9	104.3	24.3	5.19	67.8	142.3	28.6				
La4	5.56	37.0	163.2	12.3	5.31	69.7	144.1	27.6	6.01	338	160.1	1.9
La4	5.16	41.0	166.9	28.5	5.24	49.8	157.8	27.0	6.01	366	127.7	0.5
La4	5.58	25.0	223.1	38.2	5.29	84.7	113.4	31.6	6.02	376	93.8	0.8
La4	5.42	19	203.0	34.6	5.37	80.2	156.5	26.7	6.03	384	119.0	1.4
La4	5.27	45	159.4	29.6	5.24	74.4	105.6	28.5				
La4	5.19	24	376.8	25.3	5.23	63.5	108.3	24.4				
Ce1	5.35	27	1160.3	30.2	5.29	47.1	102.9	20.1	6.12	346	173.6	0.5
Ce1	4.98	38	922.6	18.8	5.32	32.6	98.8	19.0	6.02	354	152.5	0.9
Ce1	5.35	24	1331.8	34.7	5.09	61.8	114.3	20.6	6.12	393	165.5	1.3
Ce1	5.21	26	1102.8	25.4	5.14	91.1	138.5	28.2	6.06	347	147.3	1.3
Ce1	5.14	40	1235.2	23.0	5.35	84.7	133.6	25.8				

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Ce1	5.29	22	1459.6	30.9	5.31	76.8	48.9	12.7				
Ce2	5.36	29	859.7	23.4	5.24	53.8	145.4	25.8	6.14	319	107.5	0.9
Ce2	5.66	22	1134.7	29.6	5.12	62.2	120.5	19.5	6.18	324	97.1	0.9
Ce2	5.31	27	1082.6	29.8	5.55	86.2	121.2	26.4	6.22	367	133.5	-0.3
Ce2	5.10	43	1149.3	22.2	5.34	44.4	115.3	23.4	6.33	352	121.3	1.6
Ce2	5.17	35	1080.6	22.0	5.32	70.2	120.7	21.3				
Ce2	5.35	28	1145.1	28.5	5.22	73.2	71.7	21.6				
Ce3	5.32	26	681.6	23.9	5.34	76.2	181.3	25.7	6.36	380	178.3	1.3
Ce3	5.32	31	812.8	26.8	5.14	76.5	182.2	25.1	6.42	406	132.7	0.7
Ce3	5.49	17	670.3	41.8	5.25	68.0	115.8	28.4	6.31	407	35.3	0.8
Ce3	5.44	19	823.2	32.8	5.39	58.4	138.7	31.6	6.3	369	118.6	0.8
Ce3	5.41	29	892.9	27.1	5.08	74.2	138.4	26.5				
Ce3	5.21	45	882.1	20.2	5.30	78.3	128.7	26.5				
Ce4	5.59	23	151.1	28.0	5.30	77.1	214.9	28.3	6.44	362	129.2	-0.2
Ce4	5.58	22	122.1	29.7	5.14	49.3	187.3	26.8	6.27	428	118.2	0.7
Ce4	5.55	21	106.5	26.7	5.18	45.0	136.4	26.0	6.36	414	162.2	2.0
Ce4	5.12	35	113.2	21.7	5.42	72.1	176.8	28.9	6.35	400	147.7	0.0
Ce4	5.12	42	121.2	23.9	5.44	93.4	159.5	27.4				
Ce4	5.06	47	89.6	21.1	5.27	83.8	127.8	23.3				
Ca1	5.25	24	125.5	29.1	5.35	71.4	140.4	26.2	6.09	438	136.1	1.3
Ca1	5.39	18	169.8	29.5	5.34	40.9	119.6	26.7	6.14	414	146.3	3.3
Ca1	5.42	17	204.4	30.6	5.18	71.8	133.9	22.8	6.09	364	119.8	1.1
Ca1	4.76	90	114.0	15.4	5.23	66.6	156.5	25.2	5.98	378	142.5	0.9
Ca1	5.43	29	149.6	26.9	5.26	63.6	97.4	23.3				
Ca1	5.03	52	130.9	22.2	5.24	72.5	120.6	23.2				
Ca2	5.47	22	208.0	35.6	5.25	56.6	124.8	23.9	6.28	460	137.4	1.2
Ca2	5.06	55	169.8	21.6	5.01	50.8	135.2	20.7	6.27	401	0	1.6
Ca2	5.46	17	164.3	35.3	5.24	50.3	124.0	19.3	6.25	404	96.2	0.4
Ca2	5.05	48	97.0	18.2	5.21	63.6	130.6	25.9	6.13	391	144.7	0.6
Ca2	5.05	22	157.0	38.1	5.25	56.3	152.8	22.3				
Ca2	5.03	56	166.8	25.1	5.16	78.6	141.7	21.8				
Ca3	4.95	65	125.1	23.1	5.46	58.0	164.9	27.3	6.22	407	203.2	-0.3
Ca3	4.96	48	145.2	23.0	5.42	63.7	134.9	22.0	6.27	462	160.1	0.1
Ca3	5.82	23	169.4	38.9	5.62	73.3	161.0	26.8	6.04	382	116.6	0.6
Ca3	5.37	22	176.2	31.2	5.29	58.4	162.1	27.8	6.21	369	145.9	0.5
Ca3	5.17	42	150.3	23.5	5.28	84.8	178.7	23.9				
Ca3	5.28	52	146.7	24.6	5.39	67.3	191.9	24.1				
Ca4	5.58	22	134.9	35.0	4.96	93.8	126.4	21.2	6.17	421	165.9	0.8
Ca4	5.30	34	127.9	32.8	5.24	64.6	256.0	23.5	6.10	429	141.6	0.2
Ca4	5.23	56	122.2	26.9	4.88	79.3	161.6	11.4	6.25	418	212.8	-0.4
Ca4	5.19	58	135.2	24.7	5.24	58.6	171.8	23.4	6.18	445	138.1	0.6

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Ca4	5.08	66	135.8	23.1	5.27	70.5	177.7	20.6				
Ca4	4.68	85	70.3	17.0	5.00	69.4	120.4	17.8				
REE1	5.07	43	117.4	23.6	4.85	67.4	64.6	18.8	5.66	389	189.6	0.6
REE1	5.11	34	116.5	28.3	5.38	53.1	157.0	22.5	6.33	427	150.1	1.4
REE1	5.18	39	125.3	26.3	4.96	59.3	202.7	19.6	6.42	374	103.6	0.5
REE1	5.26	24	127.7	30.8	5.05	59.6	445.2	21.9	6.17	358	104.3	-1.0
REE1	4.89	57	97.4	16.8	5.15	64.3	157.7	19.0				
REE1	5.35	43	175.0	26.2	5.24	75.7	181.4	19.8				
REE2	5.48	28	80.2	27.1	5.19	100	129.4	21.0	6.11	385	104.0	-0.2
REE2	5.10	46	108.0	22.8	4.97	67.4	170.6	14.5	6.04	345	127.4	0.8
REE2	4.96	50	80.5	17.7	5.38	52.5	205.9	27.4	6.06	382	110.0	2.3
REE2	5.12	51	55.7	20.9	5.06	66.5	132.5	20.9	5.84	372	110.4	1.6
REE2	5.03	51	103.2	27.7	5.09	73.3	155.3	17.3				
REE2	4.99	62	82.2	26.2	4.85	64.2	170.8	19.7				
REE3	4.81	87	83.4	18.3	5.24	66.2	165.4	24.4	6.26	391	140.7	0.8
REE3	4.87	73	91.1	20.1	5.18	69.4	150.1	28.3	6.31	446	143.1	0.6
REE3	5.11	40	118.2	27.6	5.00	54.2	78.7	18.5	6.33	385	111.7	0.2
REE3	5.02	62	82.2	23.2	5.29	67.2	137.9	21.9	6.03	382	50.2	-0.4
REE3	5.11	56	80.6	24.4	5.66	48.8	165.5	20.7				
REE3	4.87	81.0	46.0	16.1	5.07	64.6	118.9	17.5				
REE4	5.29	62.4	163.2	20.2	5.47	107.4	193.0	24.1	5.89	411	141.2	0.3
REE4	5.06	125.8	136.6	16.5	5.44	82.9	219.2	26.4	5.99	424	122.3	0.9
REE4	4.90	96.8	152.5	15.1	5.47	98.4	112.4	22.0	5.91	418	120.9	0.9
REE4	4.96	141.7	157.1	15.3	5.27	99.5	130.5	18.3	5.82	419	114.7	1.4
REE4	5.07	129.7	128.8	16.1	5.54	93.3	218.1	22.6				
REE4	5.27	119.6	139.5	17.5	5.31	89.2	228.1	25.1				

* no data

Table C.7: Analytical data of rare earth elements content (µg g^{-1}) of maize and oilseed rape after 35 days of sowing (2006)

Treatment	Maize								Oilseed rape							
	Roots				Shoots				Roots				Shoots			
	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd
Control	1.62	2.01	0.177	0.61	0.12	0.21	<LQ	0.07	2.68	4.05	0.376	1.24	0.45	0.80	0.08	0.25
Control	1.91	3.31	0.341	1.22	0.14	0.23	<LQ	0.08	1.33	2.07	0.199	0.66	0.32	0.51	0.05	0.15
Control	0.78	1.43	0.141	0.48	0.10	0.18	<LQ	0.05	2.49	3.13	0.294	0.94	0.40	0.59	0.05	0.16
Control	1.11	1.95	0.186	0.67	0.07	0.11	<LQ	0.04	1.42	2.56	0.127	0.40	0.28	0.42	0.04	0.13
Control	1.16	2.09	0.209	0.72	0.09	0.13	<LQ	0.05	1.56	0.97	<LQ	0.32	0.40	0.46	0.04	0.14
Control					0.07	0.09	<LQ	0.04								
La1	3.19	4.03	0.380	1.31	0.10	0.12	<LQ	0.05	2.07	1.87	<LQ	0.57	0.84	0.95	0.09	0.28
La1	2.75	2.89	0.296	1.03	0.11	0.12	<LQ	0.05	3.26	4.56	0.392	1.27	0.50	0.64	0.06	0.19
La1	3.10	4.46	0.405	1.37	0.11	0.13	<LQ	0.05	5.75	6.85	0.575	1.87	0.52	0.65	0.06	0.19
La1	2.84	3.30	0.256	0.88	0.08	0.09	<LQ	0.03	0.82	0.81	0.079	0.24	0.36	0.42	0.04	0.13
La1	2.29	3.45	0.288	0.98	0.07	0.07	<LQ	0.03	1.87	2.25	0.211	0.67	0.29	0.28	<LQ	0.09
La1	1.88	3.86	0.331	1.16	0.13	0.14	<LQ	0.05	3.10	0.87	0.086	0.30				
La2	11.38	3.08	0.28	1.00	0.30	0.09	<LQ	0.04	6.08	1.00	0.095	0.33	0.43	0.48	0.05	0.15
La2	9.50	4.64	0.40	1.44	0.45	0.09	<LQ	0.04	3.78	1.90	0.094	0.32	0.44	0.22	<LQ	0.07
La2	13.49	3.24	0.28	0.98	0.33	0.12	<LQ	0.05	5.21	1.05	<LQ	0.25	0.51	0.22	<LQ	0.07
La2	10.47	1.90	0.19	0.63	0.42	0.08	<LQ	0.03	3.23	1.78	0.099	0.32	1.00	0.33	0.03	0.11
La2	9.73	3.02	0.27	0.97	0.51	0.16	<LQ	0.06	4.26	1.26	0.102	0.34	1.50	0.43	0.04	0.16
La2	8.84	2.10	0.19	0.72	0.45	0.10	<LQ	0.04					1.50	0.49	0.05	0.16
La3	31.01	3.24	0.25	0.89	0.90	0.10	<LQ	0.04	10.43	0.94	<LQ	0.23	2.84	0.97	0.10	0.31
La3	27.93	3.32	0.31	1.09	1.19	0.13	<LQ	0.05	23.44	1.02	<LQ	0.34	7.78	0.58	0.06	0.20
La3	42.13	2.80	0.25	0.92	1.51	0.11	<LQ	0.04	7.96	1.55	0.151	0.50	2.12	0.46	0.04	0.14
La3	27.65	3.43	0.31	1.14	1.00	0.20	0.02	0.08	19.95	1.03	0.092	0.32	1.89	0.31	0.03	0.10
La3	42.28	2.65	0.24	0.84	3.12	0.16	<LQ	0.06	10.56	1.79	<LQ	0.36	2.11	0.37	0.04	0.12
La3	30.77	3.75	0.30	1.07	2.03	0.20	<LQ	0.07	60.05	1.92	<LQ	0.64	6.31	0.36	0.03	0.11
La4	425.24	2.40	0.218	0.75	2.76	0.10	<LQ	0.03	80.24	1.99	0.108	0.36	18.48	0.87	0.08	0.26
La4	116.52	3.71	0.366	1.32	2.86	0.19	<LQ	0.07	114.47	1.09	<LQ	0.32	6.91	0.33	0.03	0.10
La4	240.68	2.56	0.234	0.83	1.95	0.09	<LQ	0.03	100.88	2.96	0.271	0.93	3.68	0.27	<LQ	0.08
La4	145.71	2.29	0.208	0.73	2.78	0.11	<LQ	0.04	201.68	12.93	1.044	3.37	29.51	0.61	<LQ	0.19
La4	267.83	2.64	0.217	0.78	3.30	0.09	<LQ	0.03	133.96	1.83	0.155	0.54	11.85	0.38	0.04	0.12
La4	235.89	2.55	0.244	0.85	2.21	0.09	<LQ	0.03	91.79	1.58	0.137	0.48	17.58	0.45	0.04	0.14
Ce1	2.57	3.52	0.290	1.07	0.96	0.16	<LQ	0.05	23.84	15.09	1.428	4.68	3.31	0.70	0.05	0.17
Ce1	5.42	2.51	0.180	0.63	0.42	0.10	<LQ	0.03	7.74	9.06	0.842	2.63	1.35	0.30	0.02	0.07
Ce1	1.77	3.49	0.250	0.89	0.34	0.13	<LQ	0.04	2.99	1.24	0.078	0.27	1.09	0.54	0.04	0.14
Ce1	2.24	3.24	0.240	0.88	0.29	0.14	<LQ	0.04	1.08	2.20	<LQ	0.61	1.02	0.60	0.04	0.14
Ce1	2.54	4.57	0.390	1.32	0.30	0.13	<LQ	0.04	1.23	2.20	0.115	0.41	0.88	0.55	0.04	0.13
Ce1	1.30	3.19	0.210	0.78	0.21	0.10	<LQ	<LQ	1.02	2.02	0.134	0.46	0.71	0.44	0.03	0.11

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Ce2	2.36	10.43	0.360	1.24	0.28	0.44	<LQ	0.05	1.28	6.16	0.146	0.51	0.70	0.52	0.03	0.08
Ce2	1.17	8.89	0.240	0.85	0.21	0.30	<LQ	0.04	0.95	5.72	0.135	0.46	0.61	0.97	0.03	0.09
Ce2	1.75	10.60	0.300	1.04	0.45	0.44	<LQ	0.06	0.89	4.17	<LQ	0.23	0.48	1.43	0.03	0.11
Ce2	3.16	10.18	0.499	1.64	0.94	0.40	<LQ	0.07	0.66	1.97	<LQ	0.18	0.62	1.13	0.04	0.12
Ce2	1.90	7.43	0.339	1.19	0.21	0.65	<LQ	<LQ	2.14	7.24	<LQ	0.75	0.98	1.54	0.06	0.19
Ce2	2.10	16.56	0.363	1.22	0.13	0.25	<LQ	0.03	0.85	6.84	0.124	0.43	0.42	0.87	0.03	0.09
Ce3	0.77	26.27	0.137	0.48	0.11	0.45	<LQ	0.03	1.71	16.50	0.172	0.58	0.44	2.33	0.03	0.09
Ce3	1.16	23.76	0.208	0.70	0.09	0.39	<LQ	<LQ	1.71	20.57	0.184	0.62	0.79	2.05	0.10	0.33
Ce3	1.50	23.12	0.277	0.92	0.14	0.75	<LQ	0.05	1.35	15.49	0.141	0.46	0.30	1.54	<LQ	0.07
Ce3	2.11	28.76	0.350	1.16	0.36	1.27	<LQ	0.06	1.42	15.48	0.158	0.51	0.40	2.91	0.04	0.14
Ce3	1.72	28.13	0.309	1.04	0.76	1.31	<LQ	0.23	0.71	10.97	0.088	0.30	0.60	1.46	0.03	0.10
Ce3	3.59	14.23	0.516	1.66	0.23	0.77	<LQ	0.04	1.05	17.46	0.160	0.54	0.65	6.95	0.07	0.26
Ce4	1.81	51.63	0.261	0.83	0.10	0.94	<LQ	0.03	2.78	46.02	0.145	0.49	0.28	3.73	0.03	0.07
Ce4	1.62	138.29	0.292	1.01	0.10	1.01	<LQ	0.03	1.17	33.61	0.110	0.36	0.33	6.39	0.03	0.09
Ce4	1.44	91.89	0.243	0.86	0.15	2.33	<LQ	0.06	0.85	21.01	0.127	0.40	0.21	1.68	<LQ	0.06
Ce4	1.34	56.73	0.175	0.63	0.13	1.91	<LQ	0.07	0.44	29.31	<LQ	0.23	0.37	3.74	0.03	0.09
Ce4	1.55	89.64	0.160	0.52	0.07	0.89	<LQ	0.03	0.92	26.88	0.119	0.38	0.24	4.51	<LQ	0.08
Ce4	1.80	94.64	0.270	0.89	0.09	1.33	<LQ	0.04	0.67	41.71	<LQ	0.33	0.37	8.34	0.04	0.13
Ca1	4.29	7.29	0.650	2.16	0.07	0.33	<LQ	<LQ	1.61	2.54	0.108	0.38	0.25	0.83	<LQ	0.08
Ca1	1.59	4.93	0.230	0.82	0.11	0.80	<LQ	0.06	1.30	2.64	0.211	0.71	0.23	0.86	0.03	0.08
Ca1	2.99	5.14	0.470	1.55	0.07	0.22	<LQ	0.03	0.82	1.45	0.097	0.32	0.24	0.58	<LQ	0.07
Ca1	1.54	2.38	0.220	0.75	0.10	0.58	<LQ	0.04	1.42	1.92	0.157	0.52	0.20	0.46	<LQ	0.06
Ca1	2.23	3.72	0.340	1.15	0.18	0.23	<LQ	0.05	0.69	0.93	0.063	0.21	0.20	0.54	<LQ	0.06
Ca1	1.75	3.86	0.290	1.07	0.10	0.19	<LQ	0.04	1.15	1.24	0.105	0.35				
Ca2	1.64	2.75	0.270	0.98	0.13	0.21	<LQ	0.04	1.36	2.62	0.215	0.69				
Ca2	1.62	2.63	0.230	0.81	0.09	0.15	<LQ	0.03	2.26	3.13	0.270	0.85				
Ca2	1.35	2.44	0.230	0.83	0.09	0.25	<LQ	0.05	0.86	1.65	0.143	0.50				
Ca2	1.46	4.50	0.220	0.80	0.09	0.21	<LQ	0.04	1.27	1.45	0.138	0.47				
Ca2	1.49	2.57	0.200	0.69	0.12	0.28	<LQ	0.06	2.11	3.89	0.318	1.04				
Ca2	2.31	4.07	0.390	1.30	0.08	0.21	<LQ	0.04	0.76	1.68	0.133	0.45				
Ca3	1.51	2.39	0.220	0.80	0.09	0.21	<LQ	0.05	0.56	1.08	0.107	0.30	0.65	1.27	0.12	0.35
Ca3	1.18	2.59	0.240	0.85	0.07	0.18	<LQ	0.04	1.26	1.89	0.173	0.54	0.21	0.36	0.03	0.10
Ca3	1.34	3.23	0.280	1.01	0.08	0.12	<LQ	0.03	1.04	1.40	0.127	0.45				
Ca3	2.97	5.70	0.460	1.54	0.06	0.10	<LQ	0.04	3.75	1.10	0.111	0.29				
Ca3	1.26	2.65	0.260	0.90	0.06	0.10	<LQ	0.04	4.39	5.97	0.558	1.83				
Ca3	3.81	6.19	0.580	2.00	0.08	0.15	<LQ	0.06	0.97	1.77	0.151	0.50				
Ca4	1.39	3.01	0.300	1.05	0.05	0.10	<LQ	0.03	0.77	1.28	0.118	0.40	0.25	0.39	0.03	0.11
Ca4	1.10	2.03	0.200	0.72	0.09	0.17	<LQ	0.06	0.67	1.00	0.085	0.28	0.20	0.31	0.03	0.08
Ca4	1.23	2.57	0.230	0.81	0.06	0.11	<LQ	0.04	0.92	1.63	0.132	0.46	0.23	0.36	0.03	0.10
Ca4	1.45	2.73	0.260	0.91	0.09	0.17	<LQ	0.05	0.81	1.46	0.118	0.39	0.32	0.47	0.04	0.13
Ca4	1.19	2.45	0.240	0.84	0.09	0.17	<LQ	0.06	1.23	2.20	0.204	0.70	0.29	0.37	0.03	0.10

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Ca4	1.38	3.84	0.280	0.98	0.07	0.12	<LQ	0.04	8.05	10.13	0.878	2.87				
REE1	2.07	3.94	0.360	1.25	0.09	0.16	<LQ	0.06	1.67	1.97	0.196	0.64	0.33	0.47	0.04	0.13
REE1	1.72	3.54	0.330	1.14	0.10	0.17	<LQ	0.06	2.83	3.60	0.339	1.10	0.47	0.62	0.06	0.19
REE1	2.97	3.62	0.330	1.13	0.08	0.13	<LQ	0.05	2.50	1.61	0.149	0.50	0.35	0.46	0.04	0.12
REE1	1.75	3.51	0.350	1.24	0.08	0.16	<LQ	0.05	1.49	2.84	0.262	0.86	0.29	0.34	0.03	0.10
REE1	2.11	3.97	0.380	1.34	0.09	0.15	<LQ	0.05	2.49	4.08	0.373	1.19	0.37	0.50	0.04	0.14
REE1	3.36	6.18	0.590	1.99	0.08	0.13	<LQ	0.05	1.03	2.13	0.178	0.60	0.44	0.57	0.05	0.16
REE2	8.00	13.92	1.380	4.51	0.53	0.95	0.10	0.31	5.85	8.56	0.785	2.59	2.52	4.17	0.42	1.25
REE2	5.78	10.02	0.990	3.22	0.38	0.64	0.07	0.21	7.68	13.15	1.257	3.99	0.75	1.13	0.11	0.35
REE2	6.55	11.39	1.110	3.64	0.40	0.68	0.07	0.22	3.58	5.35	0.519	1.65	0.55	0.73	0.07	0.20
REE2	4.07	7.39	0.730	2.46	0.19	0.28	0.03	0.09	2.91	4.08	0.390	1.20	0.62	0.93	0.09	0.27
REE2	6.05	10.32	1.010	3.38	0.45	0.76	0.08	0.25								
REE2	7.10	12.76	1.270	4.21	0.41	0.70	0.08	0.24								
REE3	38.72	50.80	4.818	15.57	1.66	2.42	0.25	0.78	8.64	12.84	1.23	4.08	1.54	2.42	0.25	0.75
REE3	45.96	58.34	5.583	18.22	1.41	1.83	0.18	0.58	18.78	25.34	2.39	7.64	3.17	4.99	0.50	1.54
REE3	66.00	90.84	8.611	27.43	1.19	1.72	0.18	0.55	20.44	28.88	2.74	8.92	6.01	9.72	0.97	3.01
REE3	34.60	47.96	4.629	14.83	1.46	2.27	0.24	0.73	12.61	16.88	1.59	5.21	3.57	5.22	0.51	1.60
REE3	56.15	70.78	6.679	22.45	0.96	1.10	0.11	0.34	16.25	22.99	2.15	6.91	1.63	2.71	0.24	0.72
REE3					1.11	1.71	0.18	0.54	18.23	24.59	2.33	7.55	2.86	4.75	0.47	1.42
REE4	239.86	314.83	29.837	95.56	2.02	2.29	0.22	0.73	74.82	92.08	8.43	27.19	2.14	3.47	0.34	1.05
REE4	252.41	320.66	29.650	96.65	2.94	3.51	0.36	1.14	86.62	108.14	10.17	32.19	7.21	12.20	1.23	3.80
REE4	325.12	414.20	39.132	122.69	2.32	2.37	0.24	0.81	102.97	136.39	12.75	40.65	11.99	21.30	2.19	6.55
REE4	359.64	444.97	42.493	135.75	2.94	3.07	0.32	1.13	74.38	93.02	8.73	29.24	3.90	6.60	0.66	2.02
REE4	557.22	698.63	65.234	210.58	5.84	5.18	0.51	1.82	116.06	145.83	13.619	42.86	9.20	16.32	1.72	5.17
REE4	319.59	412.99	39.377	127.36	4.12	5.56	0.57	1.83	186.26	243.14	22.70	69.42	11.45	20.78	2.17	6.47

Appendix

Table C.8: Analytical data of rare earth elements content (µg g^{-1}) of maize and oilseed rape after 66 days of sowing (2006)

Treatment	Maize								Oilseed rape							
	Roots				Shoots				Roots				Shoots			
	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd
Control	4.36	9.13	0.93	3.41	0.126	0.173	< *	0.063	11.29	21.91	2.24	7.95	0.156	0.234	*	0.083
Control	4.32	8.95	0.91	3.35	0.066	0.280	*	0.055	8.21	18.51	1.70	6.13	0.567	1.009	0.102	0.339
Control	4.50	9.28	0.95	3.48					8.19	16.38	1.65	5.92	0.121	0.187	*	0.066
Control	4.18	8.64	0.88	3.22					13.37	25.71	2.53	9.01	0.122	0.199	*	0.066
Control	4.33	9.28	0.92	3.34					8.76	16.90	1.69	6.05	0.159	0.248	*	0.084
Control	3.72	7.74	0.78	2.85					7.39	15.41	1.53	5.60				
La1	2.74	5.50	0.58	2.10	0.070	0.097	*	*	11.08	21.02	2.14	7.73	0.217	0.244	*	0.087
La1	4.85	9.11	0.94	3.43					16.47	26.58	2.67	9.44	0.431	0.468	0.047	0.154
La1	2.43	4.56	0.47	1.70					10.07	18.36	1.81	6.55	0.205	0.268	*	0.100
La1	5.95	11.18	1.14	4.17					10.33	18.36	1.83	6.57	0.166	0.206	*	0.076
La1	5.45	10.77	1.13	4.07					12.09	21.75	2.20	7.98	0.245	0.307	*	0.100
La1	2.79	6.48	0.59	2.05					10.40	17.43	1.74	6.34	0.279	0.373	*	0.148
La2	8.60	8.23	0.83	3.06	0.202	0.138	*	0.064	23.86	19.23	1.95	7.03	0.858	0.230	*	0.080
La2	9.24	7.79	0.80	2.91	0.186	0.266	*	0.085	23.60	18.40	1.85	6.70	1.167	0.671	0.066	0.227
La2	9.07	7.28	0.77	2.82	0.098	0.066	*	*	24.93	17.65	1.78	6.40	0.861	0.396	*	0.158
La2	10.64	10.42	1.07	3.84	0.168	0.173	*	0.063	22.69	17.58	1.75	6.14				
La2	9.86	9.40	0.97	3.50					21.10	15.12	1.48	5.40				
La2	6.38	6.98	0.71	2.57					24.60	19.39	1.81	6.55				
La3	27.24	10.34	1.04	3.86					77.21	20.05	1.97	7.02	2.609	0.287	*	0.108
La3	22.35	5.53	0.57	2.08					56.87	13.83	1.32	4.69	6.928	1.067	0.111	0.363
La3	18.27	4.50	0.45	1.66					84.07	16.19	1.55	5.55	2.278	0.311	*	0.119
La3	18.40	7.31	0.74	2.72					75.44	23.44	2.29	8.17				
La3	21.38	9.57	0.97	3.56					80.19	16.67	1.48	5.30				
La3	20.21	8.55	0.87	3.12					78.85	17.87	1.69	6.02				
La4	38.15	6.91	0.69	2.55	2.014	0.155	*	*	104.58	19.16	1.91	6.79	6.515	0.392		0.147
La4	69.47	9.16	0.91	3.33	0.774	0.130	*	*	178.24	17.69	1.74	6.12	5.480	0.402	*	0.167
La4	55.67	10.11	1.03	3.71	0.585	0.092	*	*	106.18	17.55	1.69	6.08	8.074	1.225	0.132	0.432
La4	53.05	10.09	1.02	3.70	0.608	0.127	*	*	99.63	16.62	1.63	5.81				
La4	56.86	9.32	0.94	3.44					131.92	17.76	1.78	6.32				
La4									136.72	20.48	1.96	7.03				
Ce1	4.52	9.87	0.99	3.61	0.137	0.235	*	0.073	10.16	19.12	1.91	6.82	0.311	0.348	*	0.112
Ce1	4.95	10.74	1.07	3.89	0.054	0.097	*	*	8.25	17.48	1.66	6.02	0.350	0.604	*	0.145
Ce1	3.73	8.38	0.82	2.98	0.073	0.125	*	*	10.44	21.59	2.09	7.60	0.267	0.383	*	0.126
Ce1	2.17	4.87	0.48	1.69	0.111	0.192	*	0.066	6.51	17.66	1.32	4.80	0.072	0.085	*	<LQ
Ce1	3.92	8.86	0.87	3.15	0.093	0.176	*	0.064	8.42	17.89	1.70	6.17				
Ce1	4.50	10.14	1.00	3.65					7.16	16.10	1.42	5.10				
Ce2	4.21	12.67	0.94	3.46	0.059	0.112	*	*	8.08	24.44	1.65	5.93	0.239	0.802	*	0.149

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Ce2	3.12	10.43	0.69	2.47	0.059	0.134	*	*	8.96	22.67	1.54	5.53	0.246	0.584	*	0.103
Ce2	4.42	14.44	0.97	3.53	0.070	0.160	*	0.050	6.42	21.34	1.30	4.64	0.145	0.652	*	0.075
Ce2	3.17	10.50	0.71	2.57	0.060	0.492	*	0.075	8.57	26.22	1.77	6.44	0.149	0.622	*	0.085
Ce2	4.62	16.40	1.04	3.74	*	0.129	*	*	9.83	31.24	2.01	7.24	0.117	0.558	*	0.061
Ce2	3.50	12.88	0.81	2.92					10.44	29.26	1.92	6.98	0.157	0.730	*	0.088
Ce3	4.69	25.17	1.05	3.79	0.052	0.225	*	*	9.14	58.12	1.94	6.85	0.187	2.804	*	0.119
Ce3	2.25	20.77	0.53	1.90	0.046	0.199	*	*	8.78	85.23	1.78	6.35	0.105	1.249	*	0.057
Ce3	5.28	29.95	1.19	4.26	0.055	0.247	*	*	10.56	63.22	2.18	7.70	0.168	1.934		0.103
Ce3	3.98	25.27	0.90	3.22	0.056	0.278	*	0.056	10.33	52.59	1.74	6.16	0.171	1.971	*	0.111
Ce3	4.83	37.56	1.08	3.92	0.097	0.501	*	0.075	8.65	71.17	1.82	6.34	0.248	1.994	*	0.119
Ce3	5.60	30.88	1.26	4.55					8.06	53.71	1.61	5.72	0.212	2.203	*	0.142
Ce4	4.15	97.76	0.97	3.40	0.058	0.358	*	*	8.18	131.40	1.66	5.91	0.128	3.208	*	0.069
Ce4	5.20	39.53	1.15	4.17	0.086	0.782	*	0.066	8.17	108.72	1.74	6.14	0.298	2.742		0.136
Ce4	4.38	49.65	0.98	3.49	0.052	0.701	*	0.043	9.81	130.49	2.00	7.11	0.140	2.499	*	0.083
Ce4	3.11	38.27	0.70	2.51	*	0.423	*	*	9.78	108.39	2.09	7.37	0.144	3.448	*	0.077
Ce4	4.82	49.21	1.06	3.79	*	0.618	*	*	10.85	97.61	1.91	3.30	0.209	3.919	*	0.126
Ce4	3.75	33.00	0.82	2.95	0.054	0.440	*	*	8.81	131.67	1.80	6.42	0.213	4.491	*	0.124
Ca1	3.76	8.24	0.83	3.03	*	0.097	*		8.66	17.46	1.74	6.28	0.142	0.185	*	0.053
Ca1	4.56	9.71	1.02	3.65	*	0.126	*	*	8.77	16.99	1.71	6.21	0.207	0.346	*	0.108
Ca1	3.74	8.14	0.83	3.00	*	0.099		*	7.51	14.80	1.48	5.39	0.127	0.150		0.050
Ca1	3.92	8.36	0.84	3.02	0.078	0.146	*	*	7.96	16.14	1.62	5.89	0.086	0.115	*	LQ<
Ca1	3.93	8.43	0.86	3.12	*	0.076	*	*	8.27	16.83	1.69	6.16	0.127	0.171	*	0.059
Ca1	4.13	8.79	0.91	3.29	*	0.064	*	*	9.26	18.43	1.88	6.90	0.121	0.174	*	0.063
Ca2	4.50	9.56	0.99	3.58	*	0.082	*	*	6.26	12.52	1.25	4.49	0.121	0.183	*	0.062
Ca2	5.02	10.45	1.12	4.04	0.121	0.290	*	0.085	9.33	19.02	1.94	7.04	0.203	0.315	*	0.102
Ca2	5.54	11.78	1.23	4.50	*	0.081		*	7.94	14.84	1.47	5.35	0.128	0.188		0.064
Ca2	3.84	7.98	0.81	2.98	*	0.059	*	*	8.60	16.92	1.69	6.13	0.129	0.215	*	0.081
Ca2	4.25	8.91	0.90	3.37	0.059	0.108	*	*	7.39	13.62	1.36	4.96	0.204	0.352	*	0.120
Ca2	4.81	10.12	1.04	3.82					8.15	16.43	1.66	6.04	0.112	0.179	*	0.054
Ca3	4.47	9.63	0.99	3.54	*	0.046	*	*	11.16	22.36	2.32	8.39	0.174	0.307	*	0.108
Ca3	5.23	10.97	1.14	4.10	0.048	0.081	*	*	9.20	19.21	1.93	7.06	0.194	0.337	*	0.107
Ca3	6.23	12.88	1.37	4.94	*	0.079	*	*	9.46	18.99	1.92	6.85	0.101	0.142	*	0.046
Ca3	4.51	9.55	0.98	3.55	*	0.062	*	*	7.37	14.86	1.51	5.39	0.088	0.135	*	0.047
Ca3	4.64	9.72	0.99	3.68	*	0.064	*	*	6.96	13.66	1.41	5.18	0.142	0.249	*	0.093
Ca3	8.41	17.62	1.83	6.72					8.71	17.86	1.76	6.32	0.102	0.142	*	0.051
Ca4	4.61	9.70	1.02	3.73	*	0.060	*	*	7.83	16.22	1.61	5.85	0.069	0.095	*	LQ<
Ca4	3.90	7.92	0.81	2.95	*	0.048	*	*	7.78	16.04	1.56	5.59	0.285	0.484	0.047	0.147
Ca4	5.07	10.73	1.11	4.05	*	0.050	*	*	7.57	15.70	1.54	5.59	0.090	0.119	*	0.040
Ca4	3.80	7.92	0.82	2.95	0.100	0.191	*	0.081	7.37	13.72	1.32	4.72	0.102	0.156	*	0.054
Ca4	4.98	10.39	1.06	3.90	0.063	0.104	*	0.045	5.73	11.20	1.10	3.92	0.129	0.225	*	0.078
Ca4	6.29	13.43	1.38	5.01					13.51	23.75	2.35	8.29	0.120	0.181	*	0.065

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REE1	5.10	10.63	1.10	4.04	*	0.059	*	*	11.10	21.98	2.24	8.02	0.236	0.354		0.123
REE1	4.38	9.12	0.94	3.34	0.081	0.116	*	0.066	17.33	30.35	3.04	10.28	0.437	0.696	0.071	0.235
REE1	6.23	13.01	1.35	4.82	*	0.051	*	*	10.08	17.45	1.72	6.02	0.174	0.274	*	0.096
REE1	3.88	8.13	0.84	2.99	0.049	0.093		*	8.48	16.28	1.58	5.57	0.130	0.185	*	0.070
REE1	4.93	10.12	1.04	3.67	0.060	0.095	*	*	9.72	19.32	1.94	6.88	0.180	0.255	*	0.079
REE1	3.83	7.98	0.82	2.95	0.057	0.105	*	*	10.54	20.59	2.08	7.31	0.235	0.372	*	0.133
REE2	8.07	15.81	1.62	5.61	0.154	0.260	*	0.085	26.76	48.18	4.80	15.63	0.774	1.125	0.115	0.340
REE2	10.29	20.05	2.04	7.02	0.172	0.279		0.093	26.12	43.87	4.18	13.31	0.809	1.225	0.126	0.392
REE2	11.29	22.04	2.26	7.64	0.117	0.183	*	0.061	28.35	47.72	4.81	16.06	0.529	0.806	0.086	0.265
REE2	10.32	20.14	2.04	6.83	0.128	0.198	*	0.058	28.60	49.36	4.89	15.87	0.856	1.235	0.125	0.374
REE2	9.65	18.79	1.91	6.48	0.186	0.225	*	0.073	30.74	52.02	5.25	16.69	0.914	1.258	0.128	0.385
REE2	10.94	21.32	2.16	7.32	0.149	0.290	*	0.092	38.64	61.96	6.41	20.61	0.857	1.152	0.117	0.351
REE3	33.46	55.13	5.38	17.72	0.590	0.689	0.068	0.209	93.84	150.86	14.88	46.16	2.199	3.183	0.354	1.225
REE3	46.60	78.99	8.01	25.61	0.608	0.675	0.067	0.227	116.97	180.09	17.41	54.23	2.975	4.610	0.495	1.645
REE3	21.07	36.62	3.70	12.05	0.340	0.386	*	0.127	92.39	153.34	15.13	47.95	2.657	4.016	0.434	1.394
REE3	32.58	57.23	5.80	18.82	0.323	0.399	*	0.124	138.97	204.93	19.52	59.76	1.653	2.518	0.294	1.039
REE3	28.93	49.31	4.87	16.16	0.208	0.256	*	0.085	91.47	140.15	13.41	41.68	3.146	4.979	0.525	1.664
REE3	41.33	71.28	7.30	23.18	0.492	0.655	0.066	0.208	90.56	140.49	13.66	41.74	2.219	3.221	0.346	1.201
REE4	62.93	99.62	9.93	31.74	1.091	1.365	0.142	0.438	139.13	215.01	20.45	64.20	3.838	5.935	0.661	2.218
REE4	114.54	176.61	17.50	55.37	1.471	1.544	0.149	0.482	209.30	305.20	28.17	85.76	4.254	6.127	0.663	2.238
REE4	81.43	126.06	12.30	39.39	1.262	1.286	0.121	0.425	146.60	208.82	19.21	58.28	2.217	3.223	0.355	1.228
REE4	219.07	308.92	30.71	96.61	2.925	2.976	0.290	0.943	195.01	280.31	26.02	79.71	3.947	5.851	0.625	2.036
REE4	138.42	207.58	20.82	65.68	1.584	1.611	0.155	0.524	166.13	239.68	22.36	68.64	3.980	5.783	0.618	2.022
REE4	107.39	163.22	16.07	51.45	1.730	1.985	0.196	0.657	124.81	164.26	15.29	46.80	4.226	7.019	0.753	2.326

* < lower limit of quantitation

Appendix

Table C.9: Analytical data of essential nutrient concentrations of maize after 35 days of sowing (2006)

Treatment	Roots									Shoots								
	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	-------Concentrations (%) ------				-------- Concentrations (µg g^{-1}) -------					------Concentrations (%)------				--------Concentrations (µg g^{-1}) ---------				
Control	0.27	3.63	0.67	0.32	572	78	179	15	9.02	0.27	7.90	0.60	0.31	186	133	67	15	9.79
Control	0.34	3.59	1.00	0.42	1067	113	161	24	< *	0.28	7.79	0.67	0.31	320	152	59	18	11.44
Control	0.25	4.33	0.67	0.32	1081	84	184	16	*	0.28	7.88	0.56	0.29	191	154	61	15	8.57
Control	0.41								*	0.27	7.37	0.72	0.34	164	172	76	16	11.67
Control	0.32	4.89	1.15	0.53	620	118	182	20	*	0.28	7.24	0.78	0.33	207	157	64	16	11.86
Control		4.95	0.88	0.42	596	97	210	25	*	0.28	7.93	0.77	0.32	134	187	127	18	13.10
La1	0.28	3.48	0.70	0.36	955	134	145	24	7.62	0.27	7.37	0.59	0.32	134	157	121	17	9.50
La1	0.38	4.29	0.90	0.39	840	132	253	22	*	0.30	7.70	0.80	0.34	158	188	101	19	9.87
La1	0.27	3.94	0.93	0.45	720	173	133	16	*	0.27	7.54	0.71	0.35	147	203	73	16	10.49
La1	0.32	4.46	0.80	0.36	825	121	101	25	*	0.27	7.46	0.61	0.30	152	144	70	16	11.42
La1	0.28	4.40	0.71	0.40	783	124	151	20	*	0.27	8.27	0.66	0.33	123	170	67	16	9.93
La1	0.33	3.83	0.81	0.42	768	134	118	16	6.47	0.28	8.34	0.61	0.33	128	165	69	17	11.34
La2	0.29	3.99	0.85	0.40	758	126	116	19	*	0.28	7.85	0.72	0.34	145	164	66	18	8.51
La2	0.35	4.10	0.88	0.38	1050	140	166	32	*	0.29	7.57	0.72	0.32	131	162	61	19	9.12
La2	0.27	3.84	0.61	0.27	630	82	147	18	5.61	0.26	8.05	0.55	0.32	139	135	56	16	9.17
La2	0.32	4.58	0.92	0.50	489	123	124	21	*	0.28	7.43	0.71	0.33	141	156	61	17	10.86
La2	0.32	4.04	1.02	0.46	727	140	129	19	8.34	0.28	7.79	0.73	0.33	147	161	67	23	10.31
La2	0.29	4.10	0.80	0.42	579	135	188	20	8.84	0.27	7.50	0.64	0.35	124	175	59	18	9.56
La3	0.27	4.11	0.91	0.40	692	150	132	17	7.79	0.28	7.46	0.71	0.34	134	193	54	16	10.07
La3	0.26	4.24	0.79	0.34	827	135	174	19	*	0.29	8.01	0.61	0.34	149	159	49	17	10.28
La3	0.30	4.25	0.91	0.42	634	163	101	17	8.36	0.27	8.26	0.63	0.31	135	191	54	17	12.09
La3	0.37	4.28	0.85	0.33	918	162	177	22	17.17	0.31	8.05	0.78	0.32	153	174	88	18	9.11
La3	0.29	4.51	0.74	0.35	640	140	142	18	7.08	0.28	8.10	0.62	0.30	167	165	68	18	9.20
La3	0.30	4.35	0.74	0.36	784	136	123	18	7.52	0.28	7.50	0.58	0.32	144	176	60	18	10.99
La4	0.50	6.14	1.09	0.45	609	333	118	36	*	0.31	7.72	1.07	0.37	169	242	77	20	11.64
La4	0.33	4.79	0.87	0.41	921	161	183	20	6.74	0.29	8.28	0.67	0.30	192	160	60	18	8.20
La4	0.33	5.03	1.11	0.48	543	204	211	26	7.87	0.28	8.01	0.86	0.41	117	168	63	17	10.93
La4	0.28	5.22	0.76	0.35	456	110	134	17	8.02	0.27	8.32	0.64	0.34	133	144	55	17	9.16
La4	0.28	3.88	0.87	0.42	537	185	137	20	10.37	0.29	7.07	0.82	0.36	124	197	56	17	10.02
La4	0.27	4.16	0.80	0.40	594	171	120	21	*	0.27	7.09	0.89	0.33	126	196	60	17	10.68
Ce1	0.34	4.20	0.74	0.34	779	131	161	20	*	0.30	7.98	0.69	0.32	140	165	75	19	9.64
Ce1	0.34	5.06	1.18	0.58	578	189	64	24	8.99	0.27	7.50	0.96	0.38	140	210	54	18	13.96
Ce1	0.29	4.48	0.72	0.37	701	108	169	18	7.38	0.28	7.97	0.62	0.33	143	177	55	18	9.48
Ce1	0.29	4.80	0.91	0.44	802	135	171	18	7.86	0.29	7.91	0.74	0.34	136	179	58	19	11.10
Ce1	0.28	4.89	0.85	0.44	577	130	154	35	*	0.27	7.64	0.63	0.32	147	177	45	17	11.81
Ce1	0.29	4.51	0.76	0.38	599	110	98	19	6.94	0.29	7.41	0.61	0.32	119	178	46	18	11.15
Ce2	0.37	4.86	0.97	0.48	763	184	180	27	*	0.31	7.69	0.83	0.36	155	205	51	18	12.50

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Ce2	0.33	4.52	0.84	0.42	706	137	114	18	8.59	0.28	7.77	0.72	0.34	147	181	83	17	10.39
Ce2	0.34	4.55	0.74	0.37	632	134	144	18	7.23	0.30	8.04	0.64	0.32	158	193	63	18	10.24
Ce2	0.34	4.20	0.81	0.38	743	131	93	25	8.22	0.27	7.59	0.64	0.30	176	163	56	20	10.49
Ce2	0.31	5.46	0.91	0.48	2077	243	101	34	*	0.28	7.92	0.60	0.31	262	197	53	21	16.36
Ce2	0.31	4.32	0.74	0.32	843	130	87	22	16.62	0.29	7.64	0.68	0.32	140	186	62	16	13.25
Ce3	0.32	4.25	0.77	0.36	626	140	136	18	7.36	0.29	8.32	0.62	0.33	129	176	61	18	10.56
Ce3	0.33	4.35	0.81	0.35	636	136	114	18	8.29	0.29	8.08	0.55	0.33	137	160	53	17	7.76
Ce3	0.34	4.86	0.91	0.38	659	129	183	19	7.56	0.30	8.12	0.79	0.36	156	180	73	17	9.65
Ce3	0.29	4.26	0.80	0.39	773	166	95	30	*	0.29	7.69	0.61	0.32	214	164	54	26	11.05
Ce3	0.35	5.14	0.83	0.37	797	183	135	22	8.17	0.30	7.73	0.70	0.31	267	183	53	19	10.14
Ce3	0.30	4.22	0.84	0.37	679	149	120	25	*	0.27	7.54	0.62	0.29	150	159	47	17	11.28
Ce4	0.42	5.27	1.60	0.58	746	325	318	32	*	0.31	8.33	0.93	0.34	144	226	75	19	15.98
Ce4	0.39	4.98	0.98	0.41	922	209	196	19	8.99	0.29	8.37	0.87	0.36	106	238	62	19	11.19
Ce4	0.36	4.67	0.78	0.38	685	170	174	19	*	0.28	8.26	0.70	0.34	107	224	59	19	11.58
Ce4	0.32	4.54	0.83	0.41	523	158	109	17	6.87	0.27	7.86	0.59	0.30	101	196	50	16	13.95
Ce4	0.33	5.05	0.99	0.53	408	221	114	19	*	0.26	7.93	0.80	0.35	99	222	76	17	13.27
Ce4	0.35	3.88	1.23	0.58	809	292	92	26	*	0.28	7.08	0.89	0.34	145	239	72	16	12.60
Ca1	0.32	5.13	0.52	0.29	768	154	79	23	*	0.29	8.57	0.54	0.32	121	144	55	14	9.84
Ca1	0.33	4.96	0.76	0.36	742	119	161	17	*	0.29	8.65	0.62	0.33	133	171	59	15	7.88
Ca1	0.30	4.76	0.71	0.35	645	132	127	17	6.44	0.28	8.29	0.65	0.34	91	162	56	14	10.09
Ca1	0.40	5.26	0.90	0.51	590	125	87	14	13.52	0.26	7.95	0.64	0.31	138	153	56	17	11.83
Ca1	0.34	4.35	0.76	0.33	729	104	118	19	7.50	0.28	8.11	0.55	0.31	90	153	54	16	9.83
Ca1	0.31	4.33	0.84	0.39	719	116	91	18	7.78	0.28	7.85	0.58	0.29	125	132	54	17	9.83
Ca2	0.37	5.10	0.87	0.39	738	128	202	14	13.46	0.31	8.22	0.75	0.37	125	156	78	18	10.61
Ca2	0.35	4.49	1.04	0.47	1087	111	117	17	10.50	0.27	7.81	0.73	0.31	126	161	59	17	12.95
Ca2	0.27	3.87	0.73	0.34	630	85	127	14	8.12	0.27	8.18	0.60	0.35	109	127	58	16	12.02
Ca2	0.31	3.92	0.89	0.42	652	104	160	13	*	0.28	7.82	0.56	0.29	99	147	77	20	12.73
Ca2	0.36	5.13	1.01	0.39	747	141	196	14	*	0.28	8.01	0.56	0.30	109	163	59	19	11.16
Ca2	0.39	5.06	1.02	0.41	786	161	162	37	*	0.30	7.82	0.69	0.32	129	167	65	23	13.15
Ca3	0.34	4.18	0.89	0.41	655	119	106	15	*	0.30	8.34	0.62	0.30	119	127	52	18	9.50
Ca3	0.39	4.57	0.94	0.36	704	112	171	17	7.47	0.30	8.02	0.65	0.28	109	136	59	21	9.90
Ca3	0.31	4.34	0.81	0.33	981	113	135	14	7.20	0.26	8.00	0.74	0.34	107	134	58	19	10.36
Ca3	0.31	4.02	0.88	0.34	630	107	125	12	7.10	0.30	7.94	0.69	0.31	259	153	67	19	11.43
Ca3	0.32	4.16	0.97	0.34	691	107	110	13	6.71	0.30	8.09	0.71	0.33	164	143	59	23	12.84
Ca3	0.34	4.43	1.03	0.42	850	156	103	22	7.18	0.31	8.04	0.73	0.33	180	162	57	21	13.63
Ca4	0.37	5.35	1.11	0.37	802	124	200	15	*	0.29	8.50	0.78	0.33	134	146	59	20	11.10
Ca4	0.48	6.51	1.19	0.42	612	157	251	16	8.36	0.34	8.36	1.01	0.30	134	187	71	19	13.54
Ca4	0.31	4.75	1.51	0.37	713	124	95	17	8.52	0.28	7.30	0.77	0.29	110	150	54	20	13.15
Ca4	0.38	5.61	0.93	0.38	613	122	290	19	7.26	0.29	8.36	0.93	0.37	126	170	69	24	11.44
Ca4	0.31	4.95	1.25	0.41	651	132	99	17	*	0.28	7.74	0.89	0.30	125	161	54	20	13.35
Ca4	0.34	4.04	1.21	0.41	591	152	94	16	*	0.27	7.24	0.89	0.29	119	155	54	21	14.92

Appendix

REE1	0.37	5.27	0.89	0.40	696	130	208	16	7.47	0.30	8.32	0.60	0.33	128	176	62	28	11.90
REE1	0.30	5.24	0.84	0.36	715	104	156	13	*	0.28	7.91	0.61	0.29	103	151	56	27	12.06
REE1	0.30	5.34	0.90	0.41	576	138	147	15	6.41	0.30	9.43	0.77	0.30	96	159	54	21	14.42
REE1	0.29	4.78	0.80	0.39	858	110	144	13	6.85	0.28	8.47	0.58	0.33	390	132	51	18	11.55
REE1	0.35	4.68	1.02	0.42	832	150	171	18	6.34	0.29	7.73	0.81	0.32	185	199	61	26	13.75
REE1	0.32	4.75	0.90	0.34	962	172	224	22	7.53	0.31	8.17	0.80	0.36	111	197	64	24	11.63
REE2	0.29	4.40	0.88	0.37	764	115	171	16	7.26	0.29	8.14	0.75	0.37	127	146	93	21	11.46
REE2	0.31	4.92	0.74	0.34	542	103	140	13	7.08	0.31	8.73	0.67	0.32	126	165	79	21	11.69
REE2	0.29	4.40	0.67	0.32	660	102	125	14	6.92	0.31	8.28	0.58	0.29	106	145	57	20	10.77
REE2	0.32	4.83	1.01	0.44	705	113	153	13	*	0.31	8.15	0.75	0.31	134	150	59	21	14.37
REE2	0.34	3.40	0.70	0.39	736	131	139	15	*	0.30	8.61	0.66	0.32	165	158	57	20	12.46
REE2	0.29	4.52	0.72	0.36	671	110	129	13	8.14	0.31	8.04	0.63	0.31	145	155	58	28	11.47
REE3	0.34	4.10	0.91	0.40	738	169	127	18	7.77	0.29	7.55	0.67	0.28	143	156	58	19	13.02
REE3	0.31	4.32	0.87	0.40	655	177	134	14	*	0.29	7.92	0.69	0.28	137	162	57	20	16.43
REE3	0.32	3.39	0.58	0.39	699	152	154	14	*	0.31	7.91	0.69	0.31	141	159	59	19	11.89
REE3	0.32	3.82	0.68	0.41	598	137	148	13	7.71	0.30	8.00	0.64	0.28	145	160	58	20	12.83
REE3	0.31	3.95	0.72	0.41	562	176	142	12	*	0.30	7.95	0.73	0.31	118	176	59	21	13.36
REE3	0.29	3.99	0.66	0.43	768	108	143	22	13.80	0.30	7.76	0.68	0.29	118	150	55	20	16.10
REE4	0.31	3.69	1.10	0.40	1064	239	133	21	11.58	0.31	7.44	1.00	0.32	115	204	69	34	14.64
REE4	0.30	4.49	0.99	0.39	746	272	146	23	10.33	0.29	7.34	0.84	0.30	119	214	85	60	14.55
REE4	0.29	4.73	0.95	0.40	698	289	115	13	*	0.30	7.15	0.83	0.31	104	273	60	20	15.71
REE4	0.32	4.19	1.14	0.42	740	284	139	38	*	0.31	6.60	1.07	0.31	110	267	83	20	15.32
REE4	0.33	4.19	0.88	0.42	639	393	157	19	*	0.29	6.90	0.98	0.36	130	310	98	27	19.23
REE4	0.33	3.88	0.91	0.40	1033	249	105	22	11.24	0.30	6.73	0.83	0.32	121	200	84	30	13.57

* < lower limit of quantitation

Appendix

Table C.10: Analytical data of essential nutrient concentrations of oilseed rape after 35 days of sowing (2006)

Treatment	**Roots**									**Shoots**								
	S	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**	**S**	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
	-------Concentrations (%)------				**--------Concentrations (µg g^{-1}) -------**					**------Concentrations (%)------**				**--------Concentrations (µg g^{-1}) ---------**				
Control	0.36								< *	0.97								30.13
Control	0.37	3.99	0.30	0.09	945	89	90	19	*	0.99	9.15	1.36	0.50	134	189	121	19	27.24
Control	0.39	4.38	0.33	0.11	802	92	77	18	61.85	1.01	9.24	1.63	0.49	125	196	91	19	27.71
Control	0.32	4.35	0.24	0.10	1272	97	90	81	24.44	1.03	8.59	1.59	0.43	119	210	106	19	28.59
Control	0.32	4.49	0.44	0.12	695	87	72	25	*	0.90	8.69	1.48	0.45	126	201	91	18	28.87
Control		4.54	0.37	0.10	494	66	75	7			9.43	1.63	0.43	126	198	94	18	
La1	0.43	5.11	0.27	0.16	486	83	91	11	*	0.93	9.32	1.60	0.48	175	201	101	20	31.74
La1	0.31	4.57	0.39	0.11	720	103	81	19	*	0.95	9.13	1.42	0.45	129	222	113	18	31.23
La1	0.34	4.52	0.22	0.14	662	76	141	21	*	0.91	9.26	1.67	0.50	128	249	105	14	29.38
La1	0.36	4.91	0.53	0.13	358	85	130	11	17.98	1.03	9.97	1.56	0.52	121	217	97	13	32.08
La1	0.31	4.69	0.42	0.11	349	80	144	9	18.41	0.87	8.72	1.43	0.45	97	206	102	15	28.40
La1	0.31	4.80	0.46	0.12	395	102	94	7	17.50	0.88	8.25	1.29	0.43	121	204	85	12	27.10
La2	0.33	4.77	0.40	0.11	418	82	66	10	16.41	0.92	8.35	1.44	0.47	88	199	85	11	28.27
La2	0.32	4.65	0.40	0.11	364	91	65	8	16.70	0.92	8.42	1.36	0.45	79	215	91	12	28.98
La2	0.33	5.10	0.36	0.13	291	94	73	9	21.12	0.91	9.27	1.43	0.46	114	217	137	12	30.39
La2	0.32	4.55	0.37	0.12	391	89	78	12	19.78	0.87	8.77	1.31	0.45	134	200	111	11	27.60
La2	0.35								18.54	0.84								27.46
La2		4.42	0.47	0.11	326	92	63	9			7.41	1.48	0.44	140	212	94	11	
La3	0.30	4.61	0.36	0.11	325	76	51	7	*	0.88	8.45	1.33	0.45	125	206	78	11	26.03
La3	0.31	4.38	0.36	0.12	484	96	56	21	*	0.89	9.33	1.35	0.45	168	221	92	18	29.00
La3	0.29	4.30	0.23	0.09	326	79	64	16	*	0.88	9.08	1.33	0.45	126	222	105	16	31.80
La3	0.33	4.52	0.38	0.12	471	98	55	9	17.65	0.97	8.26	1.37	0.49	109	225	93	22	28.59
La3	0.37	4.59	0.26	0.10	567	104	71	10	*	1.06	9.86	1.57	0.45	92	248	104	18	30.47
La3	0.42	4.54	0.25	0.14	742	145	110	14	*	1.09	9.02	1.85	0.45	136	293	124	22	32.56
La4	0.34	5.04	0.41	0.12	516	105	55	8	18.75	1.01	9.32	1.76	0.54	161	279	105	13	32.95
La4	0.33	5.35	0.25	0.11	534	97	64	28	*	1.15	10.68	1.61	0.53	99	280	120	19	33.45
La4	0.29	4.59	0.36	0.10	811	132	74	9	18.00	0.98	9.55	1.53	0.52	112	304	106	14	31.60
La4	0.48	4.07	0.69	0.18	3113	267	344	80	*	1.06	8.08	1.68	0.54	192	351	121	15	37.98
La4	0.35	4.82	0.33	0.12	708	137	73	10	*	1.05	9.99	1.62	0.59	120	399	114	13	33.36
La4	0.31	4.56	0.31	0.11	689	116	74	43	*	1.29	11.11	1.74	0.54	186	326	102	14	35.55
Ce1	0.48	4.98	0.39	0.16	1039	149	175	21	*	1.51	12.18	3.45	0.92	194	562	215	19	50.85
Ce1	0.27	4.63	0.33	0.13	482	76	57	11	*	0.94	10.64	1.87	0.62	89	212	127	14	35.00
Ce1	0.32	5.08	0.29	0.10	588	99	95	12	*	1.04	9.81	1.70	0.54	120	266	120	14	30.28
Ce1	0.37	4.81	0.13	0.10	697	116	76	12	*	0.93	8.16	1.45	0.53	117	253	91	13	33.36
Ce1	0.34	4.82	0.35	0.12	531	98	67	7	*	1.09	9.52	1.58	0.52	118	249	104	14	31.88
Ce1	0.41	5.37	0.66	0.16	498	135	75	8	*	1.06	9.11	1.53	0.51	136	249	108	11	30.50
Ce2	0.32	4.44	0.42	0.11	576	89	54	10	17.83	1.01	9.32	1.82	0.53	90	221	89	10	29.63

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Ce2	0.34	4.46	0.32	0.11	400	108	64	9	21.03	1.06	9.52	1.81	0.54	124	278	97	13	33.73
Ce2	0.36	5.03	0.38	0.11	174	87	58	10	19.65	1.10	9.46	1.79	0.52	127	238	82	11	34.48
Ce2	0.31	4.69	0.11	0.10	0	73	52	16	*	1.01	9.76	1.33	0.46	123	225	91	13	30.42
Ce2	0.48	4.59	0.19	0.19	0	138	131	19	*	1.05	10.19	1.96	0.56	128	306	117	15	40.04
Ce2	0.43	4.75	0.69	0.15	284	149	73	8	24.13	0.93	8.93	1.46	0.39	107	213	96	10	31.64
Ce3	0.32	4.81	0.48	0.11	408	85	94	10	16.53	1.06	9.89	1.51	0.56	103	218	90	11	31.63
Ce3	0.39	4.75	0.73	0.14	404	128	109	9	20.02	0.99	9.23	1.47	0.48	104	238	93	12	30.82
Ce3	0.31	4.57	0.37	0.10	377	102	67	14	17.55	0.91	9.62	1.52	0.48	83	226	92	10	31.33
Ce3	0.34	4.70	0.44	0.12	369	102	69	10	17.66	0.93	9.59	1.35	0.49	102	205	90	12	31.67
Ce3	0.35	4.90	0.30	0.10	0	89	119	11	*	1.23	10.83	1.78	0.61	128	286	93	15	34.83
Ce3	0.31	4.73	0.39	0.10	446	103	65	15	17.70	0.96	10.39	1.37	0.48	220	208	105	11	28.73
Ce4	0.34	5.27	0.46	0.12	390	111	61	12	18.64	1.13	10.71	1.75	0.70	116	276	105	12	34.17
Ce4	0.30	4.88	0.38	0.10	215	83	56	8	16.75	1.16	11.52	1.79	0.66	130	262	132	14	35.49
Ce4	0.32	4.85	0.48	0.10	236	99	62	9	18.22	1.09	11.46	1.54	0.50	93	236	101	11	32.65
Ce4	0.34	5.08	0.33	0.10	117	94	64	8	18.15	1.15	10.42	1.88	0.60	116	31	116	13	37.82
Ce4	0.33	5.62	0.45	0.11	254	110	62	17	20.00	0.97	10.64	1.53	0.50	103	229	85	10	30.53
Ce4	0.33	4.64	0.27	0.10	169	100	65	7	*	1.20	10.89	1.57	0.55	152	232	108	11	34.24
Ca1	0.31	4.37	0.36	0.09	350	109	50	9	15.58	1.05	9.84	1.52	0.57	94	251	95	11	32.63
Ca1	0.31	4.27	0.27	0.10	499	103	70	13	*	1.03	9.91	1.44	0.45	114	208	87	9	29.30
Ca1	0.33	5.24	0.43	0.11	223	103	64	10	18.50	1.10	10.34	1.56	0.48	92	250	96	10	30.25
Ca1	0.33	5.63	0.52	0.10	291	93	55	7	16.21	0.98	9.82	1.37	0.45	95	197	80	10	29.23
Ca1	0.36	5.17	0.65	0.11	210	98	148	12	15.98	1.08	10.00	1.52	0.49	85	220	90	10	31.17
Ca1	0.32	5.07	0.51	0.10	291	101	93	9	15.75									
Ca2	0.33	4.94	0.42	0.10	284	104	100	10	17.83									
Ca2	0.30	4.84	0.44	0.10	204	81	71	9	15.42									
Ca2	0.33	5.33	0.43	0.10	441	93	66	8	16.29									
Ca2	0.32	4.93	0.49	0.10	391	91	68	9	15.31									
Ca2	0.32	4.74	0.38	0.12	522	110	93	21	*									
Ca2	0.33	4.74	0.42	0.11	467	105	67	11	16.85									
Ca3	0.32	4.69	0.44	0.11	367	90	88	11	*	1.08								32.98
Ca3	0.34	5.44	0.47	0.10	366	93	66	9	17.35	1.04								29.65
Ca3	0.36	5.00	0.46	0.11	419	106	71	12	19.59									
Ca3	0.37	5.20	0.53	0.13	311	106	64	12	21.00									
Ca3	0.36	4.58	0.48	0.12	467	108	61	19	17.11		9.88	1.65	0.48	250	245	94	11	
Ca3	0.34	5.19	0.58	0.11	470	108	56	13	16.98		9.90	1.57	0.47	232	234	82	10	
Ca4	0.35	4.51	0.52	0.10	389	104	54	11	16.54	0.96	9.03	1.74	0.46	215	246	89	10	29.20
Ca4	0.31	4.61	0.50	0.10	235	84	58	8	14.97	1.07	9.93	1.73	0.48	258	248	91	10	28.70
Ca4	0.40	5.04	0.74	0.12	475	130	81	10	15.60	1.24	10.59	1.89	0.64	293	302	121	13	30.40
Ca4	0.47	4.37	0.59	0.12	215	139	117	13	15.69	1.16								33.02
Ca4	0.36	4.79	0.57	0.12	628	134	106	18	16.19	1.30	10.57	1.95	0.74	261	297	118	11	29.23
Ca4	0.47	4.15	0.79	0.15	1362	227	141	58	*		9.57	2.04	0.58	196	297	120	14	

Appendix

REE1	0.31	4.79	0.43	0.12	320	93	60	8	15.51	1.04	9.68	1.45	0.47	252	218	86	11	28.37
REE1	0.50	4.67	0.92	0.15	352	161	124	14	*	1.24	10.30	1.73	0.53	262	239	106	13	32.82
REE1	0.31	4.11	0.30	0.09	340	106	64	36	*	1.08	9.61	1.44	0.48	241	250	91	11	29.78
REE1	0.35	4.46	0.46	0.10	530	100	62	9	15.93	0.96	8.85	1.21	0.44	186	190	81	10	27.12
REE1	0.30	4.14	0.39	0.10	507	109	59	16	14.80	0.97	9.27	1.20	0.47	200	215	104	10	28.44
REE1	0.32	4.49	0.36	0.10	302	105	83	10	21.54	1.14	10.28	1.51	0.48	223	237	97	13	31.67
REE2	0.37								*	1.21								33.70
REE2	0.35								19.39	1.10								32.15
REE2	0.65	3.64	0.00	0.12	269	89	181	36	*	1.09	10.06	1.65	0.51	371	247	108	15	30.10
REE2	0.31	1.64	0.43	0.11	1054	130	71	19	16.58	1.06	9.50	1.43	0.48	218	228	90	11	30.36
REE2		11.05	1.08	0.17	327	201	87	41			8.76	1.48	0.39	176	223	75	10	
REE2		5.10	0.40	0.10	210	92	55	16			9.32	1.39	0.45	209	223	83	10	
REE3	0.35	4.98	0.53	0.11	401	112	63	10	18.25	1.10	9.19	1.47	0.46	211	251	89	10	30.31
REE3	0.32	4.94	0.60	0.12	346	112	117	12	16.42	1.15	9.86	1.53	0.50	276	275	92	12	33.07
REE3	0.42	4.56	0.70	0.13	312	137	106	11	*	1.21	9.86	1.98	0.57	268	265	118	11	32.36
REE3	0.34	4.62	0.47	0.10	274	102	64	9	14.66	1.04	8.53	1.58	0.49	232	245	100	10	28.72
REE3	0.33	5.00	0.50	0.12	265	90	92	16	*	1.25	9.62	1.42	0.47	198	229	104	12	29.11
REE3	0.33	4.82	0.52	0.12	578	123	98	16	*	1.17	9.34	1.78	0.54	218	306	98	12	32.47
REE4	0.54	4.13	1.02	0.20	675	248	105	15	*	0.98	8.30	1.40	0.44	183	272	90	10	27.85
REE4	0.34	4.85	0.43	0.11	388	108	73	11	*	1.08	9.25	1.74	0.53	326	270	115	12	30.45
REE4	0.42	5.06	0.44	0.12	508	139	116	21	*	1.05	8.71	1.72	0.49	297	313	96	10	29.79
REE4	0.41	4.48	0.25	0.13	829	120	150	42	*	0.99	7.91	1.64	0.50	224	310	96	11	29.30
REE4	0.38	4.46	0.40	0.73	425	141	70	10	18.09	1.05	8.99	1.79	0.49	287	183	106	10	28.93
REE4	0.38	4.62	0.39	0.15	690	144	141	15	*	1.04	10.10	1.79	0.51	309	323	135	12	31.01

* < lower limit of quantitation

Appendix

Table C 11: Analytical data of essential nutrient concentrations of maize after 66 days of sowing (2006)

Treatment	Roots									Shoots								
	S	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**	**S**	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
	-------Concentrations (%)----				**--------Concentrations (µg g^{-1}) -------**					**------Concentrations (%)------**				**--------Concentrations (µg g^{-1}) ---------**				
Control	0.19	1.50	0.69	0.30	2682	478	51	16	< *	0.16								10.86
Control	0.15	1.86	0.60	0.27	2525	398	38	13	10.81	0.13								5.48
Control	0.19	1.68	0.63	0.27	2589	348	34	18	10.35									
Control	0.18	1.87	0.66	0.30	2510	451	44	16	10.27		2.89	0.63	0.19	53	348	76	10	
Control	0.19	1.76	0.79	0.47	2951	596	55	17	11.43		2.82	0.36	0.14	57	190	76	12	
Control	0.18	1.39	0.79	0.34	2453	524	54	17	10.47									
La1	0.19	1.78	0.87	0.30	1744	393	73	23	*	0.13								*
La1	0.20	1.91	1.07	0.42	2168	747	68	20	14.23		2.89	0.42	0.16	70	290	59	9	
La1	0.16	1.84	0.75	0.28	1510	375	56	23	*									
La1	0.18	1.51	0.84	0.39	2797	709	76	21	15.03									
La1	0.18	1.89	0.66	0.26	2571	328	47	24	17.83									
La1	0.20	1.68	0.89	0.37	1576	353	38	25	*									
La2	0.20	1.56	0.99	0.40	2219	576	45	22	13.73	0.15								*
La2	0.19	1.51	0.86	0.37	2121	642	45	23	14.22	0.12	2.73	0.49	0.19	85	248	68	10	*
La2	0.15	1.37	0.65	0.28	2054	239	30	22	16.51	0.11	1.79	0.32	0.20	75	71	45	9	*
La2	0.20	1.57	0.80	0.39	2637	636	47	22	14.59	0.10	2.40	0.34	0.14	76	177	50	11	*
La2	0.20	1.32	0.86	0.38	2846	549	40	29	19.58		2.06	0.40	0.16	63	143	51	9	
La2	0.17	2.00	0.88	0.39	1835	543	36	19	12.93									
La3	0.20	1.43	0.89	0.30	2536	593	44	23	15.06									
La3	0.17	1.47	0.72	0.23	1750	289	25	27	16.87									
La3	0.18	1.83	0.81	0.26	1426	387	34	21	13.57									
La3	0.16	1.42	0.82	0.25	2151	460	87	17	11.82									
La3	0.20	1.18	0.86	0.33	2422	810	76	18	13.04									
La3	0.16	1.32	0.69	0.26	2362	591	70	16	12.90									
La4	0.21								19.83	0.10								*
La4	0.13	1.71	0.88	0.28	1955	591	62	21	15.32	0.08								*
La4	0.18	1.13	0.66	0.18	2391	296	31	13	14.56	0.09	1.38	0.51	0.17	70	92	44	9	*
La4	0.16	1.19	0.72	0.20	2575	302	34	14	12.39	0.09	1.37	0.54	0.15	32	62	102	7	*
La4	0.15	0.92	0.70	0.18	2928	369	40	13	13.57		1.41	0.33	0.09	58	63	66	9	
La4		1.07	0.68	0.19	2546	481	36	11			1.26	0.34	0.12	60	93	59	11	
Ce1	0.20	1.34	0.86	0.23	2488	467	46	13	13.92	0.09	1.56	0.30	0.13	89	68	57	8	*
Ce1	0.21	1.89	0.97	0.29	2310	791	47	12	12.53	0.13	2.22	0.31	0.16	81	226	77	9	*
Ce1	0.15	1.34	0.64	0.19	2310	371	29	15	13.49	0.10	1.65	0.28	0.17	81	85	78	8	*
Ce1	0.20	1.94	0.89	0.42	1381	523	28	12	11.34	0.14								*
Ce1	0.15	1.60	0.71	0.33	2351	568	41	12	13.22	0.10	2.33	0.32	0.15	117	196	38	11	*
Ce1	0.16	1.31	0.70	0.32	2596	481	31	14	12.96		1.66	0.31	0.17	72	110	47	8	
Ce2	0.21	1.73	0.89	0.35	2547	666	40	15	14.33	0.10	1.83	0.38	0.14	98	159	45	8	*

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Ce2	0.16	1.33	0.86	0.26	2109	314	102	15	14.73	0.10	1.28	0.32	0.15	65	86	57	10	*
Ce2	0.16	1.38	0.63	0.28	2507	497	53	11	12.19	0.12	2.03	0.32	0.20	89	169	51	8	*
Ce2	0.19	2.02	0.98	0.40	2205	702	101	13	16.15	0.15								*
Ce2	0.21	2.04	0.84	0.36	2634	798	65	14	14.94	0.11	2.39	0.25	0.19	90	230	56	10	*
Ce2	0.15	1.63	0.66	0.30	2288	471	36	10	13.43		1.84	0.31	0.19	53	153	70	8	
Ce3	0.20	1.87	0.68	0.34	2508	530	41	13	13.03	0.10	1.81	0.30	0.14	75	96	50	8	*
Ce3	0.16	1.84	0.77	0.31	1675	520	45	12	12.98	0.11								*
Ce3	0.16	1.11	0.58	0.27	3238	403	35	12	14.65	0.10	1.58	0.27	0.17	73	95	50	9	*
Ce3	0.17	1.61	0.74	0.32	2512	557	36	12	13.94	0.10	1.49	0.38	0.17	46	107	42	8	*
Ce3	0.17	1.37	0.63	0.31	2837	493	35	11	12.87	0.16	1.80	0.29	0.15	86	101	79	7	*
Ce3	0.17	1.41	0.74	0.33	3169	638	45	13	17.77		2.42	0.40	0.15	149	263	99	10	
Ce4	0.16	1.67	0.59	0.24	2628	48	36	12	16.17	0.15	2.63	0.35	0.21	99	177	63	10	*
Ce4	0.17	1.27	0.81	0.34	2940	559	40	14	13.33	0.10	1.52	0.39	0.12	132	137	54	8	*
Ce4	0.16	1.21	0.67	0.26	2569	547	33	9	14.17	0.10	1.33	0.29	0.16	110	122	58	8	*
Ce4	0.23	2.07	0.91	0.37	2044	753	40	14	14.29	0.10	1.84	0.31	0.10	107	116	69	8	*
Ce4	0.19	1.75	0.85	0.35	2626	842	48	15	14.61	0.09	1.60	0.39	0.12	78	200	59	7	*
Ce4	0.18	2.11	0.87	0.33	1821	626	63	11	12.48	0.10	1.68	0.38	0.13	95	220	56	7	*
Ca1	0.18	1.25	0.74	0.32	2152	439	55	11	14.72	0.10	1.81	0.25	0.16	109	74	52	6	*
Ca1	0.16	1.14	0.65	0.27	2479	514	93	13	16.91	0.14	1.96	0.32	0.17	112	99	45	8	*
Ca1	0.14	1.08	0.56	0.25	2222	383	29	10	13.50	0.10	1.38	0.26	0.16	100	73	39	9	*
Ca1	0.21	1.96	0.77	0.48	2117	590	70	17	15.54	0.17	3.44	0.34	0.14	202	258	57	10	*
Ca1	0.17	1.52	0.76	0.29	2350	399	45	12	13.59	0.09	1.46	0.24	0.13	96	64	33	6	*
Ca1	0.15	1.13	0.68	0.31	2368	586	55	10	16.04	0.10	1.89	0.29	0.06	105	153	50	7	*
Ca2	0.14	1.36	0.68	0.26	2693	374	47	12	15.91	0.10	1.39	0.27	0.17	103	55	47	6	*
Ca2	0.18	2.16	0.87	0.36	2496	614	57	13	15.13	0.12	2.42	0.36	0.15	153	208	85	9	*
Ca2	0.17	1.25	0.89	0.31	3203	393	48	12	16.33	0.09	1.29	0.33	0.15	119	58	83	5	*
Ca2	0.20	2.24	1.02	0.49	2207	837	66	13	15.86	0.11								*
Ca2	0.16	1.50	0.65	0.26	2132	541	41	9	13.12	0.14	1.78	0.30	0.18	122	74	64	7	*
Ca2	0.19	1.67	0.62	0.35	2539	616	56	11	15.08		3.23	0.41	0.17	163	333	81	10	
Ca3	0.17	1.28	0.70	0.34	2477	567	54	13	15.51	0.11								*
Ca3	0.21	1.20	0.94	0.42	3226	769	62	13	16.26	0.09	1.70	0.40	0.13	133	218	87	7	*
Ca3	0.16	1.17	0.64	0.28	3355	423	43	12	15.20	0.11	1.27	0.38	0.14	115	132	60	6	*
Ca3	0.19	1.40	0.86	0.31	2887	425	103	11	13.64	0.10	1.62	0.43	0.15	162	158	54	6	*
Ca3	0.18	1.61	0.95	0.37	2577	578	95	13	13.03	0.12	1.56	0.42	0.14	138	192	57	6	*
Ca3	0.18	1.49	0.68	0.37	4157	857	59	11	17.02		2.01	0.45	0.14	120	264	67	6	
Ca4	0.17	1.26	0.75	0.28	2322	331	45	10	13.20	0.11	1.54	0.51	0.16	149	146	57	6	*
Ca4	0.17	1.21	0.75	0.28	2317	500	74	12	12.77	0.10	1.27	0.37	0.14	117	126	51	5	*
Ca4	0.22	1.69	1.11	0.46	3136	767	71	13	14.93	0.12	1.98	0.38	0.13	152	229	56	8	*
Ca4	0.21	1.15	1.02	0.43	1936	741	77	10	14.35	0.14								*
Ca4	0.18	1.51	0.93	0.39	3006	650	53	10	13.78	0.14	2.63	0.50	0.15	169	299	61	7	*
Ca4	0.22	1.36	0.94	0.46	3666	743	66	17	15.86		3.39	0.60	0.18	154	317	73	6	

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REE1	0.18	1.69	0.90	0.36	2518	572	54	17	13.27	0.09	1.24	0.27	0.14	151	160	53	4	*
REE1	0.15	1.73	0.75	0.29	2067	430	48	13	13.25	0.09	1.35	0.28	0.14	159	143	49	5	*
REE1	0.25	1.50	0.79	0.38	3217	664	55	16	15.03	0.11	1.67	0.28	0.13	157	201	103	5	*
REE1	0.20	1.74	0.96	0.35	2007	404	51	15	13.43	0.11	1.34	0.31	0.16	144	124	91	7	*
REE1	0.21	1.74	0.93	0.47	2282	581	50	15	13.84	0.15	3.29	0.49	0.17	216	372	82	8	*
REE1	0.17	1.47	0.83	0.30	1822	410	37	12	12.89	0.10	1.31	0.42	0.16	124	224	69	7	*
REE2	0.16	1.04	0.98	0.34	2842	411	88	14	14.40	0.10	1.54	0.35	0.17	172	132	56	8	*
REE2	0.21	1.16	0.84	0.41	3489	716	95	16	16.31	0.12	2.20	0.40	0.15	176	238	71	9	*
REE2	0.20	0.96	0.71	0.35	3500	655	77	14	15.74	0.12	1.88	0.47	0.14	145	293	66	8	*
REE2	0.16	1.02	0.71	0.37	3404	606	64	14	15.75	0.10	1.62	0.39	0.14	192	217	79	7	*
REE2	0.18	1.09	0.80	0.37	2590	546	58	13	14.75	0.10	1.72	0.43	0.15	138	220	60	6	*
REE2	0.16	0.84	0.76	0.33	3469	709	70	15	15.17	0.08	1.37	0.32	0.11	138	167	46	6	*
REE3	0.19	1.35	0.79	0.43	2601	705	64	15	15.07	0.14	2.83	0.42	0.17	188	307	75	8	*
REE3	0.21	0.98	0.96	0.56	3904	917	76	18	16.63	0.17	2.71	0.25	0.09	234	307	49	9	*
REE3	0.16	1.19	0.82	0.31	2531	438	45	11	12.33	0.10	1.77	0.25	0.13	188	167	42	6	*
REE3	0.21	0.88	0.81	0.39	3587	744	68	16	15.31	0.13	2.06	0.37	0.16	219	282	63	8	*
REE3	0.17	1.00	0.64	0.34	3440	593	53	14	14.43	0.11	1.99	0.35	0.11	164	258	63	6	*
REE3	0.20	1.08	0.81	0.44	3468	695	57	17	14.22	0.13	3.16	0.43	0.15	163	295	60	8	*
REE4	0.14	0.91	0.66	0.31	3020	779	62	12	14.55	0.11	1.95	0.37	0.12	155	301	107	7	*
REE4	0.22	1.25	0.71	0.41	3387	559	62	20	16.74	0.17	4.20	0.39	0.16	217	282	107	7	*
REE4	0.19	1.69	0.78	0.41	2554	480	60	16	13.67	0.17	3.81	0.51	0.15	186	333	92	9	*
REE4	0.25	1.27	0.82	0.42	3751	563	93	25	18.31	0.19	5.52	0.78	0.19	217	440	94	10	*
REE4	0.24	1.35	0.73	0.44	4015	448	113	23	16.69	0.21	4.56	0.40	0.13	225	302	65	9	11.80
REE4	0.22	1.21	0.71	0.40	4209	533	112	20	16.91	0.17	4.33	0.44	0.14	209	316	84	8	*

* < lower limit of quantitation

Appendix

Table C.12: Analytical data of essential nutrient concentrations of oilseed rape after 66 days of sowing (2006)

Treatment	Roots									Shoots								
	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	-------Concentrations (%)------				--------Concentrations (µg g^{-1}) -------					------Concentrations (%)------				--------Concentrations (µg g^{-1}) ---------				
Control	0.25	1.06	0.43	0.17	5177	575	98	31	23.17	0.30	3.29	0.98	0.19	215	615	108	10	13.08
Control	0.31	1.21	0.63	0.20	4899	712	109	40	24.36	0.31								10.87
Control	0.32	1.19	0.56	0.18	4489	635	91	33	22.59	0.35	3.03	1.27	0.23	245	613	99	9	11.54
Control	0.26	0.89	0.71	0.19	5665	709	83	33	24.68	0.33	3.42	1.26	0.23	198	449	89	8	9.82
Control	0.28	0.90	0.58	0.22	4685	696	93	33	24.32	0.30	3.34	1.34	0.24	185	468	92	8	10.92
Control	0.28	0.97	0.59	0.18	6959	709	97	33	24.95		3.01	1.32	0.22	63	445	82	8	
La1	0.23	0.80	0.70	0.19	6366	933	91	31	24.99	0.39	3.85	1.14	0.24	104	416	81	8	<LQ
La1	0.25	0.91	0.50	0.16	5029	593	128	33	24.04	0.22	2.61	0.97	0.16	108	490	86	7	9.67
La1	0.22	0.68	0.24	0.15	6345	616	79	26	20.72	0.31	3.37	1.12	0.21	71	549	97	10	10.36
La1	0.24	0.84	0.56	0.23	5150	640	91	33	21.91	0.24	2.69	1.12	0.19	79	443	81	6	9.87
La1	0.26	0.87	0.83	0.20	5241	963	110	38	25.05	0.29	2.85	1.28	0.22	94	506	78	7	<LQ
La1	0.26	0.80	0.36	0.21	5593	644	91	34	24.55	0.26	2.89	1.26	0.20	79	509	169	8	10.73
La2	0.20	0.73	0.40	0.20	6200	626	86	30	22.66	0.26								10.48
La2	0.18	0.63	0.36	0.17	6577	592	80	29	23.42	0.32	2.68	1.27	0.21	112	475	106	7	9.75
La2	0.30	1.05	0.77	0.21	4894	918	162	44	27.51	0.30								10.07
La2	0.31	0.86	0.73	0.20	5243	668	162	48	25.57									
La2	0.28	1.06	0.55	0.18	5181	721	109	35	23.42		3.48	1.14	0.21	103	487	95	7	
La2	0.28	0.92	0.36	0.19	5150	536	111	38	25.27		3.16	1.25	0.18	101	415	88	7	
La3	0.23	0.82	0.44	0.18	6566	650	97	34	25.81	0.34								10.62
La3	0.23	0.75	0.43	0.17	5331	786	95	35	22.96	0.30								11.75
La3	0.29	1.00	0.67	0.21	4538	799	95	32	23.66	0.34								10.77
La3	0.20	0.75	0.42	0.18	5582	756	89	28	23.19		3.11	1.22	0.21	64	470	98	7	
La3	0.23	1.06	0.47	0.21	5004	699	102	35	23.22		3.13	1.25	0.19	169	568	92	9	
La3	0.28	0.88	0.42	0.19	5908	669	94	37	24.06		3.27	1.20	0.22	169	563	94	7	
La4	0.20	0.76	0.54	0.18	5167	596	89	34	23.59	0.29								11.21
La4	0.24	0.70	0.75	0.19	5363	861	102	40	24.36	0.29								9.37
La4	0.23	0.82	0.35	0.16	5808	747	95	33	22.98	0.38	3.38	1.29	0.19	118	599	104	7	10.66
La4	0.26	0.82	0.39	0.16	5456	668	84	30	22.19		2.90	0.94	0.19	133	625	92	6	
La4	0.23	0.92	0.36	0.17	5398	716	90	32	23.63		3.20	1.10	0.19	222	568	84	10	
La4	0.26	0.86	0.32	0.17	5864	635	80	32	23.40									
Ce1	0.25	0.89	0.93	0.19	4869	956	129	32	22.94	0.38								13.83
Ce1	0.21	0.73	0.88	0.19	5920	716	146	32	21.80	0.35								11.57
Ce1	0.28	1.05	0.41	0.22	6514	714	111	38	26.06	0.38	3.83	1.13	0.22	129	473	76	7	11.36
Ce1	0.28	1.04	0.36	0.18	4852	549	100	37	22.67	0.45	3.52	1.04	0.20	138	514	86	10	11.21
Ce1	0.30	0.95	0.39	0.18	5395	559	98	38	23.00		3.48	1.28	0.22	188	553	87	7	
Ce1	0.27	0.55	0.55	0.21	5237	529	106	45	24.23		3.91	0.76	0.13	49	288	67	6	
Ce2	0.23	0.77	0.80	0.19	4947	865	92	32	22.29	0.26	2.78	1.05	0.16	127	357	79	5	10.44

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Ce2	0.25	0.92	0.50	0.16	5415	679	94	36	23.30	0.33	3.04	1.15	0.18	113	502	102	7	10.48
Ce2	0.30	0.94	0.45	0.16	4493	494	95	38	22.51	0.26	2.74	1.18	0.18	83	389	119	8	10.22
Ce2	0.21	0.71	0.51	0.17	6378	711	91	34	22.84	0.24	2.40	1.12	0.21	99	431	108	7	<LQ
Ce2	0.32	0.84	0.57	0.19	5536	824	101	46	26.92	0.31	3.19	1.06	0.19	94	486	96	9	9.86
Ce2	0.27	0.78	0.29	0.16	5520	545	83	38	23.40	0.30	3.08	1.16	0.18	106	536	104	6	10.64
Ce3	0.25	0.84	0.49	0.19	6351	628	85	34	22.75	0.36	2.68	1.09	0.20	142	389	81	6	<LQ
Ce3	0.29	0.69	0.44	0.18	6512	696	101	48	25.82	0.43	3.59	0.86	0.17	115	349	80	7	11.08
Ce3	0.25	0.77	0.39	0.19	5731	648	85	37	25.54	0.25	2.48	1.12	0.20	104	456	89	5	9.62
Ce3	0.25	0.91	0.50	0.18	5419	641	91	35	24.33	0.20	2.25	1.07	0.15	101	409	85	7	<LQ
Ce3	0.29	0.77	0.38	0.18	6852	643	119	41	25.01	0.41	3.11	1.10	0.22	98	628	105	8	<LQ
Ce3	0.25	0.79	0.41	0.16	5119	511	113	38	22.43	0.24	2.63	1.12	0.16	129	426	87	8	10.93
Ce4	0.27	0.97	0.48	0.18	5080	641	150	44	24.41	0.21	2.56	1.01	0.13	90	433	78	7	11.14
Ce4	0.27	1.01	0.59	0.18	4741	635	112	33	23.93	0.31	2.81	1.38	0.22	106	479	99	9	10.95
Ce4	0.28	0.90	0.63	0.19	6056	850	108	35	23.00	0.32	2.93	1.18	0.20	97	466	84	8	10.91
Ce4	0.25	0.88	0.43	0.18	6458	681	99	31	23.56	0.25	2.60	1.13	0.17	90	534	87	7	9.74
Ce4	0.31	0.92	0.45	0.16	3071	643	113	35	23.78	0.28	3.20	1.09	0.19	109	572	96	8	10.87
Ce4	0.28	1.00	0.36	0.19	5803	575	101	36	25.25	0.25	3.06	1.16	0.17	147	514	119	9	11.40
Ca1	0.24	0.89	0.48	0.18	4837	660	101	34	23.96	0.26	2.84	1.15	0.22	116	518	115	10	10.59
Ca1	0.27	0.94	0.67	0.19	5714	941	88	33	24.84	0.35	3.32	1.07	0.22	110	502	100	8	<LQ
Ca1	0.28	1.06	0.55	0.20	4895	708	101	36	25.78	0.30	2.91	1.21	0.19	109	507	81	7	10.02
Ca1	0.28	0.96	0.44	0.17	5283	589	92	35	24.42	0.38	3.23	1.26	0.22	80	420	84	9	10.78
Ca1	0.23	0.82	0.54	0.18	4249	668	87	31	24.12	0.27	2.77	1.23	0.19	120	528	92	8	10.23
Ca1	0.27	1.02	0.60	0.20	5838	840	100	36	24.67	0.35	3.31	1.12	0.18	58	447	81	8	10.66
Ca2	0.31	1.17	0.62	0.18	3929	767	104	33	22.40	0.33	2.82	1.16	0.17	112	480	80	8	10.28
Ca2	0.18	0.74	0.35	0.16	5080	572	86	28	21.31	0.24	2.59	1.09	0.16	112	481	86	7	9.96
Ca2	0.29	1.12	0.79	0.18	4496	840	166	42	24.35	0.32	3.04	1.10	0.18	119	442	90	9	12.37
Ca2	0.21	0.78	0.51	0.17	4948	682	128	35	22.83	0.23	2.28	1.10	0.16	112	470	84	7	11.35
Ca2	0.25	0.97	0.57	0.19	4336	715	134	28	22.75	0.34	3.23	1.14	0.21	119	536	91	9	11.17
Ca2	0.30	1.04	0.67	0.23	4672	766	103	32	24.34	0.33	3.18	1.01	0.19	75	438	79	7	9.98
Ca3	0.20	0.63	0.56	0.19	6012	745	104	33	24.46	0.31	2.56	1.19	0.17	111	468	87	8	10.97
Ca3	0.18	0.74	0.41	0.15	6204	650	91	27	21.81	0.32	2.93	1.16	0.17	59	493	88	7	10.70
Ca3	0.23	0.77	0.37	0.16	5536	662	94	34	24.67	0.22	2.47	1.04	0.13	35	451	124	6	11.02
Ca3	0.22	0.77	0.56	0.16	5461	629	96	33	23.55	0.28	2.41	1.08	0.15	50	421	104	6	11.22
Ca3	0.27	1.04	0.69	0.17	4464	861	107	33	23.00	0.38	2.97	1.27	0.23	102	480	96	9	11.98
Ca3	0.24	0.82	0.39	0.16	5677	665	95	32	22.93	0.28	2.56	1.30	0.17	90	528	98	8	11.76
Ca4	0.17	0.66	0.32	0.16	5310	587	87	27	22.48	0.28	2.54	0.97	0.13	40	393	89	7	11.85
Ca4	0.26	0.90	0.61	0.18	6842	974	102	35	25.16	0.38	2.99	1.44	0.19	92	519	95	8	11.74
Ca4	0.30	1.08	0.49	0.21	4935	588	107	37	26.34	0.33	3.11	1.17	0.15	55	409	91	7	12.99
Ca4	0.28	0.94	0.90	0.18	5455	1313	121	46	26.36	0.30	3.02	1.32	0.21	53	612	103	11	11.73
Ca4	0.35	1.12	0.75	0.18	3239	1193	115	42	24.76	0.29	2.76	1.14	0.18	77	555	74	7	11.19
Ca4	0.30	0.87	0.67	0.20	5705	1138	116	46	24.40	0.40	3.20	1.42	0.26	52	612	74	7	11.96

Appendix

REE1	0.24	0.74	0.48	0.19	7519	753	147	37	27.39	0.32	2.91	1.21	0.19	55	518	61	7	14.96
REE1	0.25	0.78	0.73	0.21	6149	861	128	35	26.77	0.35	3.32	1.26	0.24	77	502	64	8	13.55
REE1	0.28	0.90	0.68	0.19	4477	802	128	43	24.30	0.32	3.15	1.05	0.22	73	488	66	8	11.48
REE1	0.33	1.10	0.88	0.21	4182	1043	139	56	27.88	0.29	2.43	1.09	0.14	17	461	56	6	11.54
REE1	0.25	0.83	0.51	0.19	5133	753	101	36	24.97	0.33	2.88	1.12	0.20	81	511	69	6	11.92
REE1	0.27	0.97	0.46	0.19	4942	741	98	35	25.58	0.30	2.97	1.10	0.20	76	508	45	8	12.61
REE2	0.32	0.90	0.40	0.18	5285	939	120	40	26.36	0.58	4.27	1.32	0.19	87	980	120	9	18.44
REE2	0.40	1.08	0.53	0.19	3593	923	132	64	26.64	0.43	3.22	1.00	0.15	82	752	84	7	14.57
REE2	0.21	0.79	0.54	0.17	4722	609	85	25	23.67	0.38	3.18	1.06	0.19	100	519	70	9	12.89
REE2	0.32	1.00	0.59	0.21	5060	771	110	43	27.63	0.30	2.83	1.05	0.20	82	561	64	10	10.80
REE2	0.22	0.74	0.65	0.17	5059	1012	112	36	25.25	0.32	3.06	1.09	0.17	37	540	60	8	12.71
REE2	0.27	0.71	0.71	0.19	5897	1019	117	43	26.49	0.34	2.71	1.26	0.21	66	531	61	6	11.25
REE3	0.25	0.75	0.49	0.18	5287	782	95	34	24.35	0.35	2.93	1.27	0.21	68	571	68	11	12.83
REE3	0.31	0.92	0.41	0.17	5153	799	97	37	24.53	0.37	3.17	1.21	0.20	64	733	71	8	13.43
REE3	0.25	0.76	0.45	0.19	5298	772	105	32	25.37	0.34	3.02	1.39	0.21	70	698	73	8	13.87
REE3	0.34	0.97	0.76	0.22	3924	843	110	44	25.13	0.36	2.87	1.17	0.24	161	549	62	7	12.85
REE3	0.36	1.00	0.93	0.19	4804	1022	136	47	20.49	0.35	2.73	1.04	0.20	124	551	65	7	12.46
REE3	0.35	0.97	0.67	0.22	4024	811	121	36	18.05	0.34	2.96	1.29	0.20	68	547	65	7	14.31
REE4	0.23	0.76	0.35	0.19	4779	752	100	30	16.33	0.42	3.17	1.05	0.20	87	891	86	10	13.13
REE4	0.31	0.83	0.52	0.17	4899	882	146	45	19.76	0.30	2.49	1.35	0.21	110	773	82	7	12.64
REE4	0.37	1.08	0.66	0.15	3171	1185	178	44	16.25	0.46	3.33	1.01	0.19	122	784	72	7	11.50
REE4	0.37	0.91	0.67	0.15	3391	1654	160	44	16.68	0.47	3.91	1.11	0.18	89	1001	84	8	15.26
REE4	0.29	0.85	0.55	0.16	3913	997	129	42	17.40	0.32	2.88	1.23	0.17	99	620	61	7	*
REE4	0.29	0.94	0.72	0.17	3578	1215	126	38	17.15	0.27	2.71	1.06	0.16	81	565	55	9	*

* < lower limit of quantitation

Appendix

Table C.13: Essential nutrients uptake by maize after 66 days of sowing (2006)

Treatment	**Uptake by roots**									**Uptake by shoots**								
	S	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**	**S**	**K**	**Ca**	**Mg**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
	(mg pot^{-1})					**(µg pot^{-1})**				**(mg pot^{-1})**							**(µg pot^{-1})**	
Control	19.50	151.05	69.43	30.48	27.09	4.8	519.4	161.6		25.92					5.6	1.2	161.8	174.1
Control	17.69	212.70	68.42	31.14	28.91	4.6	432.9	150.0	123.8	21.23					3.2	1.3	200.5	92.9
Control	24.44	214.42	80.30	35.02	33.06	4.4	439.5	224.4	132.2									
Control	20.85	211.70	75.06	34.01	28.44	5.1	500.4	183.7	116.3		463.07	100.65	31.09	0.84				
Control	15.62	147.60	66.43	39.68	24.73	5.0	463.8	138.6	95.7		478.76	60.95	23.00	0.96				
Control	11.54	90.90	51.55	22.01	16.09	3.4	352.6	109.8	68.7									
La1	18.27	168.73	82.32	28.51	16.55	3.7	688.6	221.6		23.08					5.1	1.0	155.7	
La1	13.46	131.87	74.04	28.99	14.94	5.1	470.3	137.9	98.0		509.83	74.98	27.88	1.23				
La1	16.97	198.90	81.34	30.44	16.29	4.0	606.0	250.6										
La1	12.67	106.34	59.63	27.29	19.75	5.0	536.8	146.1	106.1									
La1	22.77	243.96	85.86	33.99	33.26	4.2	608.1	311.3	230.7									
La1	21.16	176.56	94.30	39.34	16.61	3.7	401.3	258.6										
La2	18.35	141.41	89.16	36.49	20.09	5.2	408.9	202.2	124.3	26.12					4.2	1.2	167.6	
La2	15.77	125.02	71.10	30.42	17.52	5.3	374.6	186.1	117.4	21.78	463.49	83.78	32.55	1.45	1.3	0.8	168.2	
La2	19.31	173.23	81.41	35.75	25.90	3.0	375.4	280.4	208.2	17.99	318.52	57.91	35.24	1.33	2.8	0.8	175.8	
La2	13.14	102.19	52.06	25.25	17.20	4.1	309.4	142.3	95.1	20.44	381.10	53.94	21.53	1.21	2.9	1.0	181.4	
La2	17.17	112.89	73.01	32.57	24.25	4.7	341.8	245.1	166.8		422.07	80.83	31.81	1.28				
La2	15.00	180.40	79.21	35.40	16.54	4.9	320.0	171.3	116.5									
La3	18.32	132.19	81.69	28.04	23.38	5.5	409.1	212.2	138.8									
La3	17.58	148.15	72.55	23.22	17.64	2.9	247.9	276.4	170.1									
La3	19.14	194.41	86.31	27.07	15.13	4.1	362.1	225.0	144.0									
La3	15.32	134.17	77.48	23.95	20.27	4.3	822.1	161.5	111.3									
La3	11.80	70.51	51.57	19.70	14.51	4.9	454.4	107.7	78.1									
La3	13.97	117.93	61.56	23.15	21.09	5.3	620.7	144.5	115.2									
La4										22.18					2.0	1.0	206.6	
La4	19.74	160.45	82.14	25.99	18.30	5.5	584.2	192.7	185.6	16.39					1.3	2.2	149.5	
La4	16.11	144.92	84.45	22.74	30.77	3.8	403.1	168.0	197.2	22.79	306.81	112.41	37.75	1.55	1.6	1.7	230.3	
La4	20.15	134.65	81.40	22.62	29.20	3.4	387.7	159.3	165.1	21.00	294.24	114.57	32.16	0.68	2.3	1.5	274.4	
La4	17.76	101.84	77.35	20.22	32.35	4.1	439.1	142.3	136.9		354.42	83.93	23.03	1.47				
La4	19.52	143.57	90.66	25.89	34.20	6.5	489.3	149.8	182.2		308.65	83.95	29.36	1.47				
Ce1	23.54	160.64	103.59	27.05	29.86	5.6	549.7	154.7	167.1	21.39	382.05	73.11	31.80	2.17	1.7	1.4	193.2	
Ce1	19.72	181.12	92.86	27.69	22.15	7.6	447.3	116.0	120.1	26.38	464.99	64.25	33.96	1.69	4.7	1.6	187.6	
Ce1	20.71	182.60	87.43	25.52	31.51	5.1	399.7	201.2	184.0	26.20	427.41	73.59	43.79	2.09	2.2	2.0	207.2	
Ce1	19.93	197.45	90.23	42.98	14.08	5.3	286.0	122.9	115.5	31.31					4.4	0.9	241.2	
Ce1	14.82	159.51	70.84	32.93	23.49	5.7	410.3	116.6	132.0	24.92	524.80	72.36	34.33	2.64	2.8	1.2	199.2	
Ce1	20.11	167.81	89.33	41.68	33.35	6.2	397.3	177.5	166.5		420.56	77.68	42.39	1.82				
Ce2	25.29	208.97	106.72	42.28	30.69	8.0	482.3	179.1	172.7	25.89	453.83	94.04	34.08	2.43	3.9	1.1	209.0	

Appendix

Ce2	17.77	147.15	95.63	28.77	23.33	3.5	1124.9	170.2	163.0	23.68	310.49	78.23	37.14	1.58	2.1	1.4	242.9	
Ce2	18.36	160.76	72.87	32.66	29.21	5.8	618.7	130.7	142.0	30.85	534.16	85.33	53.05	2.35	4.5	1.3	219.2	
Ce2	16.40	174.27	84.69	34.35	19.01	6.1	872.1	109.0	139.3	34.97					5.4	1.3	226.3	
Ce2	20.89	206.16	85.32	36.37	26.66	8.1	662.2	144.3	151.1	28.41	558.53	58.50	44.44	2.10	3.9	1.8	206.2	
Ce2	18.95	206.24	83.19	38.11	28.87	5.9	451.7	126.2	169.4		469.82	78.14	49.87	1.37				
Ce3	26.22	243.63	87.97	44.58	32.63	6.9	529.4	162.7	169.5	21.55	408.38	67.92	31.26	1.70	2.2	1.1	185.0	
Ce3	16.52	187.91	79.16	32.22	17.13	5.3	455.8	122.6	132.8	27.11					2.4	1.2	225.7	
Ce3	24.28	172.56	90.16	41.20	50.18	6.2	540.9	191.1	227.1	23.37	392.32	66.87	42.27	1.81	2.6	1.0	185.2	
Ce3	17.59	166.53	76.73	33.32	25.95	5.8	371.5	128.1	144.0	26.58	359.40	92.78	40.93	1.10	2.7	2.1	192.1	
Ce3	18.92	151.73	69.63	34.27	31.52	5.5	385.7	126.6	143.0	38.74	486.72	77.37	39.43	2.33	6.5	2.4	255.5	
Ce3	19.38	156.41	82.29	37.07	35.15	7.1	498.4	148.0	197.1		602.34	98.47	36.21	3.70				
Ce4	20.41	215.38	76.35	30.55	33.98	0.6	464.0	155.8	209.1	33.92	599.85	79.65	49.00	2.26	4.0	1.4	220.0	
Ce4	21.44	161.95	102.71	42.98	37.49	7.1	509.6	178.8	169.9	26.37	399.81	103.55	32.42	3.48	3.6	1.4	214.7	
Ce4	23.38	181.48	99.97	39.48	38.48	8.2	493.7	142.1	212.3	26.91	349.61	77.08	43.06	2.88	3.2	1.5	208.2	
Ce4	20.71	186.54	82.04	33.37	18.38	6.8	356.5	129.4	128.5	20.21	372.74	63.25	19.35	2.16	2.4	1.4	154.6	
Ce4	19.78	179.37	86.54	36.12	26.89	8.6	493.1	152.3	149.6	20.46	355.68	87.16	26.10	1.74	4.5	1.3	152.0	
Ce4	22.70	259.61	106.94	40.76	22.43	7.7	780.7	138.6	153.7	22.97	395.13	88.44	31.35	2.23	5.2	1.3	161.7	
Ca1	25.30	174.89	103.90	44.51	30.02	6.1	768.8	159.3	205.3	27.56	493.63	68.33	42.78	2.98	2.0	1.4	170.7	
Ca1	20.51	144.82	83.11	33.80	31.61	6.6	1185.2	171.8	215.6	34.95	507.26	83.41	44.66	2.90	2.6	1.2	202.7	
Ca1	16.99	134.11	69.02	31.00	27.60	4.8	356.6	129.7	167.7	25.96	361.97	69.22	42.89	2.62	1.9	1.0	240.3	
Ca1	9.53	89.74	35.28	21.87	9.72	2.7	319.9	77.1	71.3	22.24	443.74	43.92	18.27	2.61	3.3	0.7	130.9	
Ca1	21.25	189.09	94.48	35.55	29.31	5.0	558.2	152.0	169.5	21.40	362.39	60.84	33.51	2.38	1.6	0.8	141.0	
Ca1	12.91	97.55	58.98	27.21	20.48	5.1	473.9	82.9	138.7	23.72	468.69	72.22	14.25	2.60	3.8	1.2	174.7	
Ca2	16.19	156.49	78.36	29.54	31.07	4.3	538.8	139.2	183.6	24.02	335.89	64.31	40.80	2.49	1.3	1.1	154.5	
Ca2	15.87	189.92	76.24	31.36	21.99	5.4	503.4	113.5	133.3	25.67	498.25	74.38	31.51	3.15	4.3	1.8	184.9	
Ca2	19.68	148.43	105.23	37.22	38.05	4.7	569.2	145.9	194.0	20.90	302.17	76.23	35.31	2.77	1.4	1.9	117.3	
Ca2	16.39	184.28	84.17	40.59	18.17	6.9	545.9	106.9	130.5	28.26					2.0	1.7	196.1	
Ca2	19.61	184.48	80.21	32.22	26.23	6.7	498.5	116.7	161.4	28.61	472.54	78.98	48.39	3.25	7.0	1.7	207.4	
Ca2	18.01	160.09	59.10	33.72	24.27	5.9	534.4	104.2	144.1		674.96	85.87	35.35	3.40				
Ca3	13.51	102.40	55.79	27.59	19.87	4.5	433.1	107.8	124.4	23.39					4.7	1.9	153.0	
Ca3	15.18	85.31	66.49	29.58	22.87	5.5	437.9	90.5	115.3	21.38	368.25	86.69	29.21	2.88	3.3	1.5	144.0	
Ca3	22.73	168.80	92.94	40.81	48.55	6.1	627.8	175.4	219.9	24.35	313.15	92.43	33.79	2.83	3.5	1.2	126.0	
Ca3	23.37	172.97	106.50	38.69	35.71	5.3	1272.6	140.8	168.7	20.93	360.38	95.11	32.72	3.60	4.0	1.2	119.8	
Ca3	16.34	144.63	85.36	33.77	23.22	5.2	855.3	114.2	117.4	28.31	327.55	87.48	28.72	2.88	6.4	1.6	151.7	
Ca3	18.94	153.29	69.58	37.98	42.78	8.8	603.4	116.9	175.1		486.79	108.37	34.02	2.91				
Ca4	21.09	157.66	94.37	35.70	29.12	4.2	568.5	120.4	165.6	23.42	338.19	111.36	34.11	3.27	3.2	1.3	127.8	
Ca4	18.01	128.33	79.66	29.49	24.49	5.3	780.0	129.0	135.0	19.78	255.42	73.99	28.97	2.35	2.5	1.0	94.9	
Ca4	21.87	164.19	108.04	45.21	30.52	7.5	686.2	123.6	145.3	25.58	419.63	80.65	27.23	3.22	4.9	1.2	168.8	
Ca4	17.49	97.63	86.84	36.31	16.46	6.3	657.6	88.8	122.0	30.74					6.5	1.3	155.8	
Ca4	17.22	142.24	87.30	36.27	28.28	6.1	496.1	96.9	129.7	19.56	568.32	107.98	32.21	3.65	4.3	1.0	84.4	
Ca4	11.49	70.95	49.24	23.92	19.17	3.9	347.7	88.7	82.9		464.63	81.70	25.06	2.11				

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REE1	17.54	164.24	87.33	34.57	24.45	5.6	520.6	161.5	128.9	18.76	267.25	58.62	30.80	3.26	3.5	1.1	76.6	
REE1	16.80	193.56	83.95	32.91	23.20	4.8	538.1	144.5	148.7	20.27	296.84	62.13	30.68	3.49	3.1	1.1	112.8	
REE1	30.25	183.28	95.94	46.34	39.29	8.1	676.9	197.9	183.5	27.03	404.15	68.94	30.29	3.80	4.9	2.5	130.2	
REE1	18.20	161.33	89.36	32.78	18.64	3.8	472.1	143.3	124.8	19.14	235.45	54.58	28.56	2.52	2.2	1.6	126.9	
REE1	15.37	127.85	68.43	34.53	16.73	4.3	366.7	111.0	101.4	28.27	613.65	91.24	32.21	4.03	6.9	1.5	152.5	
REE1	18.42	162.50	91.97	33.42	20.17	4.5	409.8	135.8	142.7	23.55	316.87	101.79	39.37	3.00	5.4	1.7	170.4	
REE2	13.51	89.11	83.62	29.11	24.24	3.5	753.8	117.1	122.8	16.27	259.77	58.72	29.16	2.91	2.2	0.9	143.8	
REE2	18.96	103.18	74.18	35.90	30.91	6.3	838.5	142.9	144.5	27.50	513.96	93.18	34.95	4.09	5.6	1.7	201.4	
REE2	18.00	87.50	64.94	32.20	31.89	6.0	705.5	129.2	143.4	25.81	406.54	101.86	31.39	3.15	6.3	1.4	167.3	
REE2	14.44	90.60	63.21	32.34	30.12	5.4	564.2	127.7	139.4	25.18	391.54	94.01	33.32	4.63	5.2	1.9	167.1	
REE2	15.27	94.11	69.66	32.34	22.46	4.7	499.2	108.4	127.8	23.83	398.23	99.97	35.87	3.19	5.1	1.4	138.9	
REE2	14.81	75.27	68.28	29.81	31.15	6.4	624.1	134.3	136.3	19.50	329.28	76.40	27.15	3.30	4.0	1.1	142.2	
REE3	11.86	85.00	49.92	27.02	16.39	4.4	406.2	96.6	94.9	21.26	432.11	64.71	25.75	2.86	4.7	1.2	124.2	
REE3	13.35	61.21	60.44	34.86	24.48	5.8	478.4	111.8	104.3	31.64	514.77	47.29	17.05	4.46	5.8	0.9	168.5	
REE3	17.68	135.04	93.12	34.86	28.70	5.0	514.1	128.0	139.8	26.43	472.78	66.47	34.65	5.03	4.5	1.1	155.5	
REE3	16.79	71.24	65.40	31.94	29.13	6.0	549.6	128.3	124.3	28.11	431.20	76.85	32.63	4.58	5.9	1.3	166.2	
REE3	16.33	97.43	62.41	33.34	33.43	5.8	511.9	134.7	140.3	25.81	485.05	86.22	27.29	3.98	6.3	1.5	149.9	
REE3	11.13	59.49	44.57	24.40	19.07	3.8	313.2	94.1	78.2	18.38	462.85	62.24	21.33	2.38	4.3	0.9	115.8	
REE4	10.12	67.85	49.30	22.87	22.44	5.8	458.4	90.7	108.1	20.95	367.76	69.99	22.30	2.92	5.7	2.0	123.7	222.8
REE4	6.93	38.78	21.86	12.65	10.50	1.7	192.0	62.9	51.9	14.46	353.29	32.48	13.48	1.83	2.4	0.9	55.7	
REE4	10.05	87.32	40.21	21.19	13.23	2.5	309.1	82.7	70.8	17.80	410.06	55.38	16.09	2.01	3.6	1.0	92.1	
REE4	4.91	24.78	16.05	8.22	7.31	1.1	182.3	48.7	35.7	7.51	219.76	31.22	7.39	0.86	1.8	0.4	39.9	
REE4	6.80	38.53	20.69	12.50	11.44	1.3	321.4	65.8	47.6	17.23	381.44	33.77	10.97	1.88	2.5	0.5	75.1	
REE4	7.59	42.35	24.71	13.84	14.69	1.9	392.4	70.3	59.0	16.34	417.72	42.91	13.60	2.01	3.0	0.8	80.1	

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Table C.14: Essential nutrients uptake by oilseed rape after 66 days of sowing (2006)

Treatment	Uptake by roots									Uptake by shoots								
	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B	S	K	Ca	Mg	Fe	Mn	Zn	Cu	B
	(mg pot^{-1})					(µg pot^{-1})				(mg pot^{-1})							(µg pot^{-1})	
Control	14.00	60.17	24.17	9.60	29.25	3.3	555.3	177.7	130.9	20.20	218.72	65.21	12.46	1.43	4.1	0.7	65.1	86.9
Control	10.28	39.92	20.96	6.56	16.22	2.4	361.2	132.7	80.6									
Control	14.31	53.46	25.14	8.17	20.24	2.9	408.9	149.2	101.9	36.01	313.31	131.33	24.10	2.53	6.3	1.0	91.8	119.4
Control	12.11	41.53	33.21	8.76	26.57	3.3	389.6	156.5	115.8	30.51	312.77	114.77	21.34	1.81	4.1	0.8	76.7	89.7
Control	12.32	40.01	25.85	9.95	20.76	3.1	412.2	144.7	107.7	25.22	285.31	114.19	20.12	1.58	4.0	0.8	70.1	93.2
Control	11.58	40.01	24.43	7.57	28.67	2.9	398.8	134.1	102.8	40.91	313.20	137.11	23.02	0.66	4.6	0.9	81.0	
La1	8.59	30.56	26.61	7.22	24.19	3.5	345.5	117.6	95.0	23.49	414.41	122.63	25.97	1.12	4.5	0.9	84.6	104.1
La1	8.52	31.46	17.23	5.61	17.35	2.0	442.8	113.8	82.9	28.84	239.40	89.10	14.65	0.99	4.5	0.8	67.3	95.0
La1	12.68	39.70	13.73	9.02	37.06	3.6	463.6	151.8	121.0	25.51	354.41	118.41	21.82	0.75	5.8	1.0	103.0	103.9
La1	12.12	42.08	28.18	11.70	25.70	3.2	454.7	165.3	109.3	21.29	198.32	82.28	14.35	0.58	3.3	0.6	42.7	
La1	9.46	31.76	30.24	7.49	19.18	3.5	402.4	140.1	91.7	23.09	250.90	112.99	18.97	0.83	4.5	0.7	59.3	94.5
La1	10.03	31.22	13.95	8.41	21.93	2.5	355.7	132.9	96.2	22.68	253.64	110.40	17.97	0.70	4.5	1.5	67.1	92.0
La2	9.54	35.01	19.27	9.39	29.70	3.0	412.0	143.2	108.5	21.98						0.0	47.8	66.4
La2	9.04	31.37	17.78	8.57	32.69	2.9	397.0	145.4	116.4	30.50	182.52	86.25	14.61	0.76	4.9	1.1	68.8	103.2
La2	8.58	29.70	21.95	6.03	13.90	2.6	459.2	125.5	78.1							8.1	64.5	
La2	11.57	32.00	26.98	7.58	19.40	2.5	597.8	177.8	94.6									
La2	12.63	47.09	24.33	7.88	23.05	3.2	485.7	155.4	104.2		356.51	117.16	21.46	1.06				
La2	9.03	29.69	11.60	5.96	16.53	1.7	354.9	122.9	81.1		291.45	115.32	16.26	0.93				
La3	7.89	28.34	15.17	6.36	22.65	2.2	333.1	116.2	89.0	27.97					3.9	0.8	57.8	88.1
La3	7.57	24.74	14.30	5.78	17.70	2.6	315.3	115.8	76.2	22.83					4.3	0.7	66.1	89.4
La3	11.19	38.39	25.82	8.09	17.38	3.1	362.3	124.4	90.6	32.79					5.4	0.9	70.8	102.5
La3	8.69	31.80	17.81	7.82	23.67	3.2	375.9	116.7	98.3		258.37	101.35	17.74	0.53				
La3	9.67	44.23	19.64	8.62	20.97	2.9	427.2	148.7	97.3		238.48	94.91	14.76	1.29				
La3	10.72	33.53	16.03	7.28	22.51	2.5	358.6	139.8	91.7		311.14	113.72	21.27	1.61				
La4	8.20	31.42	22.08	7.37	21.24	2.5	366.2	139.1	97.0	21.04					4.3	0.7	52.6	80.2
La4	8.88	25.34	27.43	7.02	19.52	3.1	371.3	145.0	88.7	26.42					5.7	0.8	53.7	85.8
La4	8.64	30.99	13.19	6.15	22.01	2.8	359.4	126.4	87.1	38.43	241.63	92.11	13.56	0.84	5.7	0.8	100.4	107.8
La4	14.10	44.16	20.90	8.88	29.41	3.6	450.1	163.6	119.6		265.67	86.02	17.51	1.22				
La4	11.60	45.70	17.84	8.25	26.72	3.5	444.0	159.1	117.0		323.73	111.58	19.25	2.24				
La4	13.05	43.75	16.33	8.57	29.79	3.2	405.9	162.1	118.9									
Ce1	10.53	37.69	39.48	8.08	20.64	4.1	546.3	135.5	97.3	37.21					4.7	0.8	69.8	136.8
Ce1	9.43	32.62	39.59	8.54	26.58	3.2	657.4	142.6	97.9	32.40					4.7	0.8	89.6	106.6
Ce1	13.05	48.75	19.00	10.42	30.35	3.3	515.4	177.5	121.4	32.88	378.86	111.95	21.68	1.28	4.7	0.7	64.1	97.2
Ce1	10.28	37.67	12.85	6.40	17.56	2.0	362.8	134.3	82.1	32.04	324.56	96.06	18.09	1.28	2.1	0.5	44.8	80.4
Ce1	11.50	35.93	14.95	6.78	20.50	2.1	374.1	143.7	87.4		297.87	109.76	18.92	1.61				
Ce1	4.44	9.09	9.15	3.46	8.69	0.9	176.6	74.8	40.2		280.41	54.70	9.08	0.35				
Ce2	9.03	30.40	31.43	7.30	19.44	3.4	363.1	126.2	87.6	23.18	251.17	95.16	14.58	1.15	3.2	0.7	47.9	94.3

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Ce2	11.22	41.48	22.34	7.34	24.42	3.1	425.5	163.5	105.1	33.26	304.14	114.74	18.23	1.13	5.0	1.0	70.1	104.8
Ce2	10.19	32.45	15.44	5.58	15.50	1.7	327.7	129.5	77.6	24.83	256.49	110.91	16.53	0.78	3.6	1.1	74.6	95.8
Ce2	11.14	37.49	27.00	9.04	33.61	3.7	479.8	180.6	120.4	26.11	265.17	123.76	23.64	1.10	4.7	1.2	75.1	
Ce2	12.20	31.88	21.52	7.37	20.98	3.1	382.4	174.4	102.0	31.77	330.74	110.05	19.75	0.97	5.0	1.0	89.0	102.2
Ce2	11.22	32.90	12.32	6.93	23.35	2.3	349.0	161.9	99.0	26.78	279.55	105.60	16.18	0.96	4.9	0.9	55.2	96.5
Ce3	8.93	30.37	17.66	6.72	22.93	2.3	306.5	124.1	82.1	32.53	245.47	99.96	18.24	1.30	3.6	0.7	57.9	
Ce3	6.19	14.56	9.30	3.80	13.74	1.5	213.0	101.2	54.5	34.17	284.67	68.33	13.40	0.91	2.8	0.6	54.6	88.0
Ce3	12.85	39.31	19.87	9.59	29.34	3.3	436.2	190.2	130.8	22.16	223.18	100.36	17.65	0.94	4.1	0.8	47.4	86.6
Ce3	9.68	35.34	19.26	6.99	21.08	2.5	354.7	136.5	94.6	17.77	202.67	96.20	13.56	0.91	3.7	0.8	63.6	
Ce3	13.30	35.88	17.51	8.49	31.86	3.0	553.5	190.2	116.3	41.61	315.61	111.90	22.20	0.99	6.4	1.1	84.5	
Ce3	8.87	27.95	14.48	5.74	18.07	1.8	400.1	132.7	79.2	21.40	233.65	99.32	14.32	1.15	3.8	0.8	72.0	97.2
Ce4	8.39	29.86	14.86	5.43	15.70	2.0	464.9	135.7	75.4	17.69	212.52	83.77	11.14	0.75	3.6	0.6	61.6	92.3
Ce4	12.25	46.51	27.16	8.13	21.86	2.9	518.5	152.1	110.3	27.89	248.99	122.55	19.58	0.94	4.2	0.9	79.0	97.0
Ce4	11.20	36.08	25.30	7.80	24.40	3.4	436.5	141.1	92.7	31.63	288.04	116.32	19.15	0.95	4.6	0.8	77.7	107.1
Ce4	12.27	43.78	21.28	8.86	31.97	3.4	491.0	155.5	116.6	24.79	253.82	110.03	16.21	0.88	5.2	0.8	71.6	95.3
Ce4	7.32	21.70	10.70	3.69	7.28	1.5	268.8	82.9	56.4	25.85	295.37	100.33	17.08	1.01	5.3	0.9	74.9	100.4
Ce4	8.49	30.09	10.69	5.70	17.41	1.7	302.1	109.1	75.7	20.76	252.80	95.73	14.07	1.22	4.3	1.0	70.7	94.3
Ca1	10.87	41.21	22.28	8.14	22.35	3.1	468.9	157.3	110.7	24.62	264.30	107.12	20.00	1.08	4.8	1.1	96.0	98.4
Ca1	16.38	57.35	40.86	11.54	35.03	5.8	536.4	204.0	152.2	39.91	381.04	122.41	25.34	1.27	5.8	1.2	97.5	
Ca1	11.74	43.78	22.60	8.24	20.27	2.9	417.0	148.1	106.7	28.44	279.21	116.66	18.65	1.04	4.9	0.8	71.3	96.3
Ca1	9.86	33.44	15.38	5.91	18.33	2.0	320.3	122.9	84.7	30.94	261.50	101.71	17.52	0.65	3.4	0.7	76.3	87.3
Ca1	13.00	46.24	30.24	10.35	23.92	3.8	490.6	175.6	135.8	24.86	256.06	113.42	17.93	1.11	4.9	0.9	77.9	94.6
Ca1	12.30	45.83	27.14	8.86	26.33	3.8	450.8	160.9	111.2	34.15	323.07	109.64	17.61	0.56	4.4	0.8	81.8	103.9
Ca2	13.48	51.44	27.30	8.10	17.33	3.4	460.1	144.6	98.8	37.08	315.59	129.19	19.29	1.25	5.4	0.9	84.1	114.9
Ca2	10.40	41.43	19.52	9.24	28.60	3.2	483.0	160.4	120.0	21.32	229.77	96.31	14.34	1.00	4.3	0.8	66.5	88.3
Ca2	9.60	37.32	26.21	5.99	14.97	2.8	552.0	138.9	81.1	27.95	265.43	96.10	15.75	1.04	3.9	0.8	79.4	108.1
Ca2	10.07	37.24	24.18	8.05	23.50	3.2	609.5	166.2	108.4	19.76	199.64	96.66	13.98	0.98	4.1	0.7	65.2	99.6
Ca2	10.67	41.95	24.89	8.13	18.82	3.1	581.9	120.3	98.7	33.46	319.59	113.03	20.68	1.17	5.3	0.9	92.3	110.6
Ca2	12.80	43.88	28.09	9.73	19.62	3.2	432.7	133.5	102.2	38.01	369.81	117.92	22.25	0.87	5.1	0.9	84.9	116.0
Ca3	10.12	31.71	28.15	9.48	30.36	3.8	527.3	167.5	123.5	28.96	236.08	109.90	16.02	1.03	4.3	0.8	72.8	101.2
Ca3	9.69	38.93	21.47	8.14	32.76	3.4	481.5	142.8	115.1	29.88	272.53	107.89	16.22	0.55	4.6	0.8	68.1	99.6
Ca3	10.07	33.49	16.30	7.20	24.19	2.9	409.5	150.2	107.8	21.47	239.78	100.70	12.23	0.34	4.4	1.2	62.7	107.1
Ca3	10.73	37.59	27.32	8.00	26.65	3.1	466.5	162.1	114.9	28.36	241.01	108.24	14.61	0.51	4.2	1.0	62.9	112.3
Ca3	10.24	39.24	26.12	6.34	16.83	3.2	404.0	124.8	86.7	42.14	325.99	139.45	24.94	1.11	5.3	1.0	103.7	131.4
Ca3	9.78	33.89	15.97	6.60	23.45	2.7	393.5	131.7	94.7	25.83	240.04	121.60	16.13	0.85	4.9	0.9	72.1	110.2
Ca4	6.24	24.03	11.43	5.72	19.22	2.1	314.2	96.0	81.4	21.10	190.04	72.55	9.83	0.30	2.9	0.7	55.5	88.6
Ca4	9.02	31.03	21.07	6.34	23.47	3.3	350.3	121.0	86.3	39.99	311.13	150.24	19.80	0.96	5.4	1.0	87.8	122.3
Ca4	7.70	27.96	12.80	5.36	12.83	1.5	278.7	95.4	68.5	27.85	259.00	97.01	12.62	0.46	3.4	0.8	57.9	108.1
Ca4	11.70	38.44	37.03	7.28	22.42	5.4	497.8	188.4	108.3	33.92	338.91	147.42	23.18	0.59	6.9	1.2	119.3	131.5
Ca4	9.61	31.03	20.82	4.99	8.94	3.3	318.2	117.0	68.3	31.94	299.73	123.33	19.80	0.83	6.0	0.8	78.1	121.5
Ca4	13.48	39.65	30.71	8.96	26.01	5.2	528.4	208.9	111.3	45.47	361.37	161.03	29.09	0.59	6.9	0.8	84.1	135.3

Appendix

REE1	10.01	30.24	19.66	7.85	30.75	3.1	600.7	149.3	112.0	33.93	308.84	128.98	19.70	0.58	5.5	0.7	77.4	159.0
REE1	12.85	40.55	37.93	10.83	31.91	4.5	666.8	180.4	139.0	33.23	317.32	120.54	23.27	0.74	4.8	0.6	72.1	129.5
REE1	10.38	33.37	25.13	6.87	16.52	3.0	471.2	158.8	89.7	31.39	306.00	102.25	21.60	0.70	4.7	0.6	76.8	111.4
REE1	10.05	33.28	26.52	6.42	12.63	3.2	421.1	168.3	84.2	26.09	220.72	99.16	13.03	0.15	4.2	0.5	50.2	105.0
REE1	8.98	30.44	18.54	6.97	18.79	2.8	369.4	132.3	91.4	32.67	281.35	109.20	19.06	0.79	5.0	0.7	57.7	116.4
REE1	11.76	42.49	20.01	8.18	21.55	3.2	426.3	152.7	111.5	31.72	310.02	115.30	20.56	0.79	5.3	0.5	78.8	131.7
REE2	6.35	17.74	7.81	3.50	10.41	1.9	236.0	77.9	51.9	43.59	319.44	98.88	14.28	0.65	7.3	0.9	65.8	137.9
REE2	9.00	24.46	11.99	4.28	8.16	2.1	299.8	146.3	60.5	41.60	307.71	96.01	13.97	0.78	7.2	0.8	68.9	139.4
REE2	12.38	46.79	31.85	10.13	27.96	3.6	504.0	150.1	140.2	41.01	343.09	114.74	20.47	1.08	5.6	0.8	94.2	139.2
REE2	12.37	38.60	23.02	8.28	19.58	3.0	424.1	167.6	106.9	32.54	307.17	114.05	21.98	0.89	6.1	0.7	112.7	117.3
REE2	7.80	26.04	22.91	6.02	17.81	3.6	393.3	126.2	88.9	29.38	280.72	100.15	15.48	0.34	5.0	0.6	72.4	116.7
REE2	12.62	32.72	33.00	8.62	27.30	4.7	541.3	199.6	122.6	37.48	298.57	138.65	23.13	0.72	5.9	0.7	69.6	124.0
REE3	11.53	34.10	22.39	8.24	24.01	3.5	430.6	155.3	110.6	33.87	280.16	121.75	20.22	0.65	5.5	0.7	107.6	122.6
REE3	13.38	39.94	17.70	7.25	22.26	3.5	419.1	159.3	106.0	30.47	261.07	99.78	16.21	0.52	6.0	0.6	63.6	110.5
REE3	11.91	35.91	21.43	9.07	24.96	3.6	495.5	149.5	119.5	34.48	303.13	139.91	21.02	0.70	7.0	0.7	82.9	139.3
REE3	9.91	28.26	22.18	6.33	11.42	2.5	321.4	128.9	73.1	35.99	285.55	116.90	24.01	1.61	5.5	0.6	73.3	128.0
REE3	11.72	32.74	30.43	6.05	15.71	3.3	446.3	153.0	67.0	19.55	153.82	58.45	11.29	0.70	3.1	0.4	38.6	70.3
REE3	13.02	36.57	25.26	8.32	15.13	3.0	455.6	134.7	67.9	38.21	333.71	145.18	22.35	0.77	6.2	0.7	83.9	161.3
REE4	12.24	40.49	18.62	9.87	25.38	4.0	532.8	159.3	86.7	38.31	291.77	96.85	18.36	0.80	8.2	0.8	89.2	120.9
REE4	10.37	28.00	17.40	5.74	16.51	3.0	491.0	153.1	66.6	22.81	191.78	103.75	15.90	0.84	5.9	0.6	57.2	97.2
REE4	9.71	28.55	17.52	3.91	8.37	3.1	469.4	116.3	42.9	50.25	361.46	109.69	21.16	1.33	8.5	0.8	81.3	124.9
REE4	7.18	17.72	12.98	2.98	6.58	3.2	310.4	85.9	32.4	38.52	319.57	90.40	14.40	0.72	8.2	0.7	67.0	124.8
REE4	7.39	21.87	14.06	4.10	10.09	2.6	333.2	108.0	44.9	26.55	238.88	101.56	14.44	0.82	5.1	0.5	57.7	
REE4	8.03	25.93	19.82	4.58	9.91	0.0	348.0	106.1	47.5	32.49	330.23	129.03	18.88	0.98	6.9	0.7	106.3	

Appendix

Table C.15: Rare earth elements uptake (µg pot^{-1}) by maize and oilseed rape after 66 days of sowing (2006)

Treatment	Maize								Oilseed rape							
	Uptake by roots				Uptake by shoots				Uptake by roots				Uptake by shoots			
	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd	La	Ce	Pr	Nd
Control	44.08	92.22	9.39	34.40	2.02	2.77		1.01	63.80	123.80	12.64	44.89	1.04	1.55		1.01
Control	49.46	102.42	10.37	38.32	1.12	4.75		0.93	27.18	61.28	5.62	20.28	5.86	10.43	1.06	0.93
Control	57.53	118.50	12.16	44.48					36.93	73.87	7.44	26.69	1.10	1.71		
Control	47.40	97.84	10.00	36.47					62.72	120.59	11.85	42.25	1.04	1.70		
Control	36.30	77.78	7.71	28.00					38.82	74.88	7.49	26.81	1.66	2.58		
Control	24.40	50.76	5.10	18.72					30.46	63.50	6.29	23.08				
La1	25.97	52.19	5.46	19.93	1.23	1.71			42.12	79.89	8.14	29.36	2.33	2.62		
La1	33.41	62.78	6.47	23.66					56.82	91.69	9.23	32.56	3.95	4.29	0.43	
La1	26.24	49.23	5.05	18.39					58.79	107.25	10.55	38.26	2.16	2.82		
La1	41.98	78.91	8.05	29.45					51.52	91.61	9.13	32.77	1.22	1.52		
La1	70.55	139.32	14.58	52.65					44.26	79.62	8.04	29.20	2.16	2.70		
La1	29.45	68.25	6.19	21.63					40.78	68.31	6.81	24.86	2.45	3.27		
La2	77.80	74.53	7.54	27.70	3.43	2.35		1.08	114.27	92.13	9.33	33.66	5.85	1.57		1.08
La2	76.33	64.38	6.58	24.06	3.31	4.75		1.52	117.31	91.43	9.21	33.30	11.96	6.87	0.68	1.52
La2	114.32	91.84	9.66	35.61	1.56	1.04			70.81	50.11	5.06	18.19	7.94	3.65		
La2	69.34	67.96	6.96	25.06	3.43	3.54		1.29	83.94	65.06	6.46	22.71				1.29
La2	83.98	80.06	8.26	29.85					93.90	67.28	6.60	24.04				
La2	57.51	62.85	6.43	23.17					78.97	62.25	5.80	21.03				
La3	251.18	95.31	9.57	35.63					266.38	69.18	6.78	24.21	21.65	2.39		
La3	225.24	55.72	5.72	21.01					188.80	45.92	4.37	15.56	52.72	8.12	0.85	
La3	193.79	47.70	4.78	17.58					321.98	62.00	5.95	21.24	21.66	2.96		
La3	173.33	68.89	6.93	25.60					319.86	99.37	9.70	34.63				
La3	128.08	57.31	5.83	21.31					335.99	69.86	6.19	22.22				
La3	180.48	76.33	7.73	27.82					300.40	68.09	6.44	22.94				
La4					44.73	3.43			429.84	78.73	7.86	27.90	46.58	2.81		
La4	357.08	64.68	6.50	23.90	16.57	2.78			648.78	64.41	6.32	22.27	50.19	3.68	0.44	
La4	894.08	117.90	11.75	42.84	14.73	2.32			402.43	66.51	6.40	23.04	81.63	12.38	1.33	
La4	631.27	114.61	11.73	42.11	14.94	3.12			537.03	89.60	8.78	31.31				
La4	586.26	111.52	11.26	40.85					652.98	87.93	8.81	31.28				
La4	763.67	125.19	12.62	46.13					694.52	104.02	9.96	35.73				
Ce1	54.25	118.38	11.85	43.27	3.35	5.74		1.79	43.09	81.08	8.10	28.93	3.07	3.44		1.79
Ce1	47.46	103.04	10.29	37.30	1.13	2.03			37.03	78.47	7.44	27.05	3.22	5.57		
Ce1	50.91	114.35	11.15	40.61	1.90	3.25			48.65	100.59	9.74	35.42	2.29	3.28		
Ce1	22.15	49.62	4.85	17.26	2.51	4.33		1.48	23.56	63.92	4.77	17.38	0.51	0.61		1.48
Ce1	39.21	88.56	8.72	31.52	2.35	4.46		1.61	31.98	68.00	6.47	23.46				1.61
Ce1	57.82	130.28	12.80	46.85					11.89	26.72	2.35	8.46				
Ce2	50.76	152.70	11.33	41.70	1.46	2.78			31.77	96.06	6.50	23.31	2.16	7.24		

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Ce2	34.47	115.39	7.60	27.33	1.43	3.24			40.43	102.25	6.96	24.93	2.46	5.84		
Ce2	51.53	168.19	11.35	41.08	1.85	4.23		1.32	22.14	73.61	4.48	16.00	1.36	6.11		1.32
Ce2	27.34	90.48	6.16	22.13	1.41	11.48		1.76	45.15	138.16	9.31	33.91	1.64	6.87		1.76
Ce2	46.80	166.01	10.52	37.85		3.29			37.27	118.38	7.61	27.43	1.21	5.78		
Ce2	44.22	162.60	10.27	36.84					44.15	123.76	8.13	29.54	1.42	6.62		
Ce3	61.03	327.43	13.67	49.31	1.18	5.09			32.99	209.80	6.99	24.73	1.72	25.68		
Ce3	22.97	212.49	5.45	19.46	1.15	4.94			18.53	179.82	3.76	13.39	0.83	9.92		
Ce3	81.78	464.19	18.41	66.09	1.34	5.95			54.06	323.69	11.18	39.42	1.51	17.40		
Ce3	41.06	261.03	9.34	33.27	1.50	7.51		1.50	40.19	204.59	6.78	23.95	1.54	17.73		1.50
Ce3	53.67	417.26	12.02	43.51	2.41	12.45		1.87	40.20	330.92	8.47	29.50	2.52	20.24		1.87
Ce3	62.15	342.51	14.02	50.44					28.45	189.58	5.67	20.18	1.89	19.58		
Ce4	53.63	1263.98	12.55	43.98	1.32	8.17			25.27	406.02	5.12	18.26	1.06	26.59		
Ce4	66.26	504.06	14.66	53.19	2.26	20.63		1.73	37.69	501.21	8.01	28.31	2.64	24.29		1.73
Ce4	65.67	743.77	14.69	52.27	1.36	18.40		1.14	39.54	525.86	8.08	28.67	1.37	24.54		1.14
Ce4	27.97	344.05	6.27	22.59		8.55			48.43	536.53	10.33	36.49	1.41	33.72		
Ce4	49.39	503.87	10.90	38.84		13.76			25.72	231.34	4.53	7.82	1.93	36.17		
Ce4	46.15	406.50	10.14	36.35	1.28	10.35			26.42	395.02	5.41	19.27	1.76	37.14		
Ca1	52.45	114.93	11.52	42.24		2.65			40.03	80.68	8.06	29.03	1.32	1.71		
Ca1	58.09	123.78	12.98	46.56		3.26			53.75	104.16	10.45	38.06	2.37	3.97		
Ca1	46.40	101.14	10.25	37.26		2.58			31.09	61.26	6.12	22.31	1.22	1.44		
Ca1	18.01	38.38	3.85	13.86	1.01	1.88			27.61	56.01	5.60	20.43	0.70	0.93		
Ca1	49.06	105.13	10.78	38.92		1.88			46.57	94.76	9.54	34.68	1.17	1.58		
Ca1	35.70	76.06	7.89	28.43		1.59			41.77	83.13	8.50	31.13	1.18	1.69		
Ca2	51.89	110.32	11.40	41.35		1.99			27.62	55.20	5.50	19.81	1.35	2.05		
Ca2	44.21	92.11	9.89	35.58	2.50	5.98		1.76	52.54	107.09	10.94	39.66	1.80	2.80		1.76
Ca2	65.83	139.99	14.67	53.43		1.90			26.44	49.43	4.91	17.83	1.12	1.64		
Ca2	31.60	65.67	6.68	24.50		1.57			40.85	80.38	8.02	29.10	1.13	1.89		
Ca2	52.29	109.56	11.08	41.45	1.24	2.25			32.06	59.11	5.90	21.54	2.02	3.48		
Ca2	45.99	96.75	9.98	36.51					34.24	69.01	6.96	25.39	1.30	2.08		
Ca3	35.84	77.22	7.95	28.42		0.99			56.34	112.91	11.70	42.37	1.61	2.84		
Ca3	37.09	77.79	8.06	29.10	1.18	2.01			48.55	101.42	10.19	37.28	1.81	3.14		
Ca3	90.09	186.36	19.76	71.52		1.76			41.34	83.01	8.38	29.94	0.98	1.38		
Ca3	55.79	118.08	12.18	43.96		1.30			35.98	72.52	7.36	26.29	0.89	1.35		
Ca3	41.80	87.54	8.95	33.15		1.54			26.24	51.48	5.33	19.54	1.56	2.74		
Ca3	86.54	181.30	18.81	69.17					35.98	73.76	7.25	26.09	0.95	1.33		
Ca4	57.87	121.61	12.84	46.73		1.33			28.34	58.71	5.82	21.19	0.52	0.71		
Ca4	41.23	83.67	8.57	31.14		0.96			26.68	55.00	5.34	19.17	2.97	5.04	0.49	
Ca4	49.37	104.36	10.78	39.36		1.05			19.69	40.81	4.01	14.54	0.75	0.99		
Ca4	32.29	67.32	6.99	25.06	2.16	4.12		1.75	30.30	56.38	5.44	19.38	1.15	1.75		1.75
Ca4	46.85	97.78	9.98	36.68	0.87	1.43		0.62	15.81	30.92	3.03	10.81	1.40	2.45		0.62
Ca4	32.89	70.26	7.22	26.21					61.60	108.29	10.73	37.79	1.36	2.04		

Appendix

REE1	49.49	103.18	10.72	39.23		1.29			45.41	89.91	9.17	32.80	2.51	3.76		
REE1	49.15	102.30	10.52	37.48	1.77	2.54		1.44	89.97	157.54	15.78	53.36	4.18	6.65	0.67	1.44
REE1	76.09	158.83	16.52	58.87		1.22			37.18	64.40	6.35	22.20	1.69	2.66		
REE1	36.06	75.50	7.82	27.79	0.86	1.63			25.60	49.17	4.79	16.82	1.18	1.68		
REE1	36.14	74.18	7.62	26.93	1.11	1.76			35.56	70.73	7.10	25.18	1.76	2.49		
REE1	42.43	88.34	9.03	32.65	1.39	2.54			45.98	89.75	9.06	31.86	2.45	3.89		
REE2	68.84	134.83	13.80	47.89	2.60	4.39		1.43	52.72	94.92	9.46	30.78	5.79	8.42	0.86	1.43
REE2	91.16	177.61	18.11	62.19	4.00	6.52		2.17	59.29	99.59	9.50	30.21	7.74	11.73	1.20	2.17
REE2	102.87	200.74	20.55	69.59	2.53	3.97		1.32	167.80	282.49	28.48	95.07	5.72	8.70	0.93	1.32
REE2	91.37	178.20	18.02	60.43	3.10	4.80		1.41	110.70	191.03	18.93	61.40	9.30	13.41	1.35	1.41
REE2	83.67	162.93	16.57	56.21	4.31	5.22		1.70	108.22	183.10	18.48	58.75	8.39	11.55	1.18	1.70
REE2	98.24	191.41	19.44	65.77	3.58	6.95		2.21	178.90	286.88	29.69	95.43	9.44	12.69	1.29	2.21
REE3	210.83	347.31	33.88	111.64	8.99	10.50	1.03	3.18	426.02	684.90	67.57	209.6	21.00	30.40	3.38	3.18
REE3	292.20	495.26	50.24	160.58	11.57	12.84	1.27	4.31	505.32	777.97	75.19	234.3	24.48	37.94	4.07	4.31
REE3	238.88	415.28	42.00	136.67	9.09	10.31	0.00	3.39	435.14	722.22	71.28	225.8	26.68	40.32	4.36	3.39
REE3	264.55	464.74	47.13	152.82	6.76	8.34	0.00	2.59	404.40	596.35	56.82	173.9	16.47	25.08	2.92	2.59
REE3	281.19	479.30	47.33	157.05	5.07	6.24	0.00	2.08	299.11	458.30	43.84	136.3	17.74	28.08	2.96	2.08
REE3	227.32	392.02	40.14	127.48	7.21	9.58	0.97	3.05	340.50	528.25	51.37	156.9	25.01	36.30	3.90	3.05
REE4	467.54	740.19	73.81	235.80	20.61	25.79	2.67	8.28	738.77	1141.69	108.5	340.9	35.35	54.66	6.09	8.28
REE4	355.07	547.49	54.26	171.66	12.39	13.00	1.26	4.06	705.34	1028.53	94.93	289.0	32.72	47.11	5.10	4.06
REE4	421.81	652.96	63.70	204.03	13.59	13.85	1.30	4.58	387.02	551.30	50.72	153.8	24.07	35.00	3.86	4.58
REE4	427.19	602.40	59.88	188.40	11.64	11.85	1.16	3.75	378.32	543.81	50.48	154.6	32.29	47.86	5.11	3.75
REE4	394.49	591.59	59.33	187.19	13.24	13.46	1.30	4.38	428.62	618.37	57.69	177.1	32.99	47.94	5.12	4.38
REE4	374.79	569.63	56.09	179.56	16.70	19.16	1.89	6.34	345.73	455.00	42.36	129.6	51.47	85.49	9.17	6.34

Curriculum Vitae

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